SIGNIFICANCE OF pH VARIANCE IN PREDICTING CHEMICAL REACTION IN HOT MIX ASPHALT

by

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STATEMENT OF DISSERTATION APPROVAL

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ABSTRACT

Hot Mix Asphalt (HMA) is a combination of siliceous, calcareous, or intermediate aggregates from selected sources, blended with asphalt binders from various asphalt binder producers. These components are modified by additional additives to enhance the bonding of the binders and aggregates. Concern over moisture damage (stripping), defined as the loss of strength and durability in asphalt mixtures when the binder separates from the aggregate, has prompted years of research into a variety of failure mechanisms. Prominent in these failure mechanisms is the pH at the interface of the binder and the aggregate. This dissertation addresses the pH variance of the individual components and loose blended HMA mixes from seventeen selected material sources and two asphalt binder sources to assess the pH of any chemical reactivity. The main objective is to determine if pH variances of individual components and/or mixed HMA materials (asphalt binder, aggregate and additives) point to suspect components or combinations which are causing a chemical reaction and thus instability or moisture-induced stripping at the aggregate interface. This research may point to alkali-silica and alkali-carbonate reactivity (ASR/ACR) of aggregates as potentially contributing causes of moisture-induced damage in HMA mixes. Statistical analysis is used to interpret the interaction of the independent variables and point to contributing components correlating with the pH variance and chemical reaction. With an inexpensive pH test, prior to design, suspect components could be eliminated from consideration in the design, which could then lead to improved asphalt mixtures and longer lasting pavements.

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NOMENCLATURE

NCHRP- National Cooperative Highway Research Program

UDOT- Utah Department of Transportation

HWTD- Hamburg Wheel Tracker Device

ILS- Inter-Laboratory Study

HMA- Hot Mix Asphalt

TRB- Transportation Research Board

AAPT- Association of Asphalt Paving Technologists

AASHTO- American Association of State Highway and Transportation Officials

ASTM- American Society for Testing and Materials

SHRP- Strategic Highway Research Program

ASR- alkali/silica reactivity

ACR- alkali/carbonate reactivity

PPA- poly-phosphoric acid

pH - pH measures the concentration of hydrogen and hydroxide ions on a scale from 0 to 14, with 7.0 considered neutral. pH is a measure of acidity or alkalinity.

SPSS-IBM-21- Statistical software used to evaluate data

VIF- variance inflation factor

CHAPTER I

INTRODUCTION

The current design procedure for Hot Mix Asphalt requires the contractor to submit a mix design to a Department of Transportation testing laboratory for verification. Mix designs that fail verification have to be redesigned and verified again. This verification process is costly and time consuming. In addition, verified mix designs that have used marginal materials, when produced and placed as pavement, in a short time prematurely fail in the field, causing pavement damage and costly repairs. This research investigates pH variance as an early evaluation tool which would point to marginal materials of Hot Mix Asphalt (HMA) design mixes which may contribute to chemical reaction and thus loss of adhesion or stripping of the asphalt binder from the aggregate in the mix. This research is supported by the current theory describing adhesion of bitumen and aggregate in the presence of water, causing chemical reaction at the interface. State of Utah's materials and the availability of Utah materials for testing, including both aggregates and asphalt binders, are the source materials used in this research. These Utah materials are similar in characteristics and chemical nature as aggregate and asphalts sources used in all countries, which makes the research relevant in the industry worldwide. American Society of Testing and Materials (ASTM) and American Association of State Highway and Transportation Officials (AASHTO) preparation and test methods will be used to prepare the samples. Measured pH laboratory test values of

individual components and of HMA loose mix samples are the basis to accomplish the research. A multivariate linear regression statistical model and analysis using SPSS IBM - 21 is used to quantify the test results.

Categorical Variables

- Aggregate pit or source: the seventeen selected aggregate sources at various locations.
- Oil (type): defined by a 70-28 or 64-34 Strategic Highway Research Program grade.
- Asphalt binder (source): producer who supplied the oil.
- Hydrated lime: is an additive to the HMA mix to help increase the adhesion between the asphalt binder and the aggregate.
- PPA: Poly-phosphoric acid is an additive to the formulation of the oil.
- Time: hours the specimen was soaked in distilled water.
- Region: either north or south classification of aggregate pits.
- Formula: percentages of minerals over 5 percent, from each aggregate pit.
- The continuous variables in this study were pH (the dependent variable), phagg-boiled, SiO_2, $CaCO_3$, CaO, Al_2O_3, and MgO.
- pHagg-boiled: aggregates boiled in water and soaked for 24 hours.
- SiO_2, $CaCO_3$, CaO, Al_2O_3, MgO: chemistry of the aggregates minerals in each pit.

Objectives

- Evaluate the relationships of the components used in the HMA mixes in order to determine their individual contribution to the final pH within the HMA mixes.

- Determine if the final pH of an HMA mix is a significant predictor of chemical reaction, which may lead to moisture-induced or stripping damage and less durability in the asphalt binder/aggregate mix.

Research Questions

If pH levels are suspected to affect the durability of asphalt mixtures, then the primary research questions motivating this study are:

- Does the pH of individual components of aggregates, asphalt binder, and additives point to and isolate suspect materials which chemically react and affect the final pH value?
- Are final pH levels of mixed HMA materials (asphalt binders, additives, and aggregates) significant in predicting chemical reaction, which is suspected to affect the durability of the asphalt binder/aggregate mix?

Hypothesis

The hypotheses that followed from these questions are:

- H_o: There is no statistical linear model that predicts final pH values as a function of chemical reaction and the choice of individual components of the HMA mix.
- H_a: There is a statistical linear model that predicts final pH values as a function of chemical reaction and the choice of individual components of the HMA mix.

The main theory of this work is that variances in pH readings of mixed HMA materials (asphalt binder and aggregate) are an early predictor (with P = .05 probability confidence) of chemical reaction at the asphalt binder/aggregate interface. Mineralogy or petrography of the rock or aggregate can induce ASR/ACR reactions, which produces instability at binder/aggregate interface. Combined with the formation of gel, there is a

rise in pH at the interface between the asphalt binder and aggregate in the HMA mix, causing failure by chemical reaction that breaks the mechanical bond between the binder and the aggregate. The amount of silica content or the silica phase on the rock mineralogy as well as the amount of carbonate is assessed by the chemistry of the aggregates in the various pits.

With the final pavement layer being the most expensive layer in a highway project, the causes of moisture damage or stripping, by the associated theories and mechanisms, are of particular interest in exploring in order to provide inexpensive practical solutions for choice of HMA materials. This pH study may provide an early, inexpensive practical solution for choosing or eliminating certain HMA materials to be used in design and verification processes, while also providing a longer lasting pavement structure.

CHAPTER II

LITERATURE REVIEW

Introduction

The general subject of adhesion science is multidisciplinary, encompassing aspects of engineering as well as physical and organic chemistry. A very large and diverse technical literature on adhesions exists (Pocius 1997). A definition of 'adhesion' in its scientific context is given by ASTM D907 as "the state in which two surfaces are held together by valence forces or interlocking forces, or both." The word 'adhesion' comes from the Latin word *adhaerere*, which means 'to stick to.' 'Fundamental' adhesion refers to forces between atoms at the interface, also called 'true' adhesion. 'Practical' adhesion, on the other hand, is a term that can be used to describe the results of destructive adhesion tests, such as a tensile test. The parameter recorded reflects the fundamental adhesion at the interface as well as the mechanical response of the adhesive glue, substrate, and interfacial region. The mode of failure in tests of this nature can be adhesive (rupture of bonds between molecules of different phases), cohesive (rupture of bonds between molecules within the same phase), or mixed (Packham 1992). The research of interest in this dissertation is concerned with both fundamental and practical adhesion. Moisture damage or the loss of bond or adhesion (stripping) in HMA due to the presence of moisture, causes major problems on many roads in any country. A wealth of research exists on bitumen-aggregate adhesion and the effects of water on the adhesion

bond. The bitumen-water interface and influence of pH on interfacial activity have been studied by (Scott 1978) using electrophoresis. (Labib 1992) used electrophoreses to develop zeta potential – pH curves for selected aggregate and bitumen types. Zeta potential or electro-kinetic potential is the electric potential that exists across the interface between a hydrated particle (fixed liquid) and the bulk solution (moving liquid), i.e., a measure of stability at the interface. In addition, this quantity is sensitive to changes in the pH of the system, which is significant, since the pH of water in contact with an aggregate surface changes (Labib 1992), (Scott 1978). Up to this point, the effect of pH of the water at the bitumen-aggregate interface has not been incorporated with other interfacial factors to assess its affect quantitatively. The first question to address within the context of the current theory is whether the surface energy components of water change at different pH levels (Little 2005).

A review of the literature found that the general consensus substantiates the importance of identification of the aggregate properties and the asphalt binder characteristics that affect bond or adhesion. This analysis is needed to determine which materials are inclined toward bond or adhesion loss in any hot mix asphalt combination. Historically, six contributing mechanisms to moisture damage have been identified: detachment, displacement, spontaneous emulsification, pore pressure-induced damage, hydraulic scour, and the effects of the environment on the aggregate-asphalt system (Little 2003). However, it is apparent that moisture damage is usually not limited to one mechanism but is the result of a combination of processes. It has become necessary to seek a more fundamental understanding of the moisture damage process by carefully considering the micromechanisms that influence the adhesive interface between

aggregate and asphalt and the cohesive strength and durability of the mastic (Little 2003). Additional mechanisms include pH instability and the effects of the environment or climate on asphalt-aggregate materials systems. Several processes are presented that affect this bond. The effect of aggregate mineralogy, surface properties, and the pH at the water–aggregate interface is discussed (Little 2003). In each of the five micromechanism theories presently being studied, boundary layer, mechanical, electrostatic, chemical, and thermodynamic, the energy approach is universal, and damage-predicting models use thermodynamic parameters, such as physical measurable properties, for compliance. The pH effect influences donor-acceptor interactions which lead to unstable bonds within certain pH ranges (Little 2005). In most of the theories, pH plays a prominent factor, and research to predict adhesive bond strength in the presence of water, with specific reference to the effect of pH instability of the interface water, is an investigative interest of this research. The pH scale ranges from 0 on the acidic end to 14 on the alkaline end, a solution is neutral if its pH is 7. When the pH is 7 the water contains equal concentrations of H+ and OH- ions. Substances with pH less than 7 are acidic as they contain a higher concentration of H+ ions, and those that are higher than 7 are alkaline because they contain a higher concentration of OH- ions. The pH scale is a log scale, so a change of one pH unit means a tenfold change in the concentration of hydrogen ions. This tenfold change is significant in the results of a pH test on the HMA mixtures.

Background

More than 60 years ago, work by Gzemski (1948) showed more emphasis should be placed on the influence of pH of water on moisture damage or stripping (Little 2005). Since the 1920s, researchers have attempted to develop tests to distinguish between well

and poor-performing asphalt pavements. In 1937, the Proceedings of the Association of Asphalt Paving Technologists (AAPT) papers on asphalt binder-aggregate adhesion and problems with moisture sensitivity addressed the same issues seen today with stripping (Saville 1937). Tests developed to determine moisture damage or stripping fall into two major categories: those conducted on loose asphalt-aggregate mixtures and those conducted on compacted mixes.

The static immersion and the boil test, both conducted on loose mixtures, were among the first tests introduced to the paving industry. This was followed by introduction of the immersion–compression test in the late 1940s. This test was conducted on compacted specimens and was one of the first tests to become an ASTM standard in the mid-1950s. Research in the 1960s brought considerable awareness to asphalt pavement technologists of the significant effects of climate and traffic on moisture damage. The significance of these factors was emphasized through the work of researchers such as Johnson (1969), Jiminez (1974), Little (2003), Lottman (1978), and Schmidt and Graf (1972). Lottman did extensive work which resulted in his laboratory test becoming the most accepted test in the paving industry. This test (Lottman Test) was modified by (Tunnicliff and Root 1982).

Review of papers from a National Seminar -Topic Two on the Chemical and Mechanical Processes of Moisture Damage in Hot-Mix Asphalt Pavements had the following papers presented, which were derived from the terms and research describing moisture damage. They discussed the main stripping mechanisms: Detachment, Displacement (the process of displacement can proceed through changes in the pH of the water at the aggregate surface that enters through the point of disruption), Film Rupture,

Spontaneous Emulsification, Pore Pressure, Hydraulic Scour, and pH Instability. Papers by (Scott 1978) and (Yoon 1987) demonstrated that asphalt–aggregate adhesion is strongly influenced by the pH of the contact water. (Kennedy et al. 1982) investigated the effect of various sources of water on the level of damage that occurred in a boiling test. (Fehsenfeld and Kriech undated) observed that the pH of contact water affects the value of the contact angle and the wetting characteristics at the aggregate–asphalt interface region. (Scott 1978) observed that the value of interfacial tension between asphalt and glass peaked at intermediate pH values, up to about 9, and then dropped as pH increased. (Yoon 1987) found that the pH of contact water increased with duration of contact and was aggregate-specific, and the values stabilized after about 5 to 10 minutes of boiling. Yoon determined that the coating retention in boiling tests decreased as pH increased. (Kiggundu and Roberts 1988) point out that these results indicate that stabilization of the pH sensitivity at the asphalt– aggregate interface can minimize the potential for bond breakage, provide strong durable bonds, and reducing stripping (Table 1).

Table 1- Proposed Relationships between Theories of Adhesive Bond Loss and Stripping Mechanisms (After Kiggundu and Roberts 1988)

		THEORY								
		Mechanical Interlock			Chemical Reaction			Interfacial Energy		
	Proposed Operating Mode	P	C	P-C	P	C	P-C	P	C	P-C
Stripping Mechanism	**Detachment**	S						S	W	
	Displacement					S		S		
	Spontaneous Emulsification				S	W				
	Film Rupture	S								
	Pore Pressure	S								
	Hydraulic Scouring	S								
	pH Instability					S				S

P = Physical
C = Chemical
P-C = Physical – Chemical
S = Primary Contributor
W = Secondary Contributor

Tarrer (1996) concluded that (a) the bond between asphalt and aggregate depends on surface chemical activity, (b) water at the aggregate surface (in the field) is at a high pH, (c) some liquids used as antistrips require a long curing period (in excess of about 3 hours) to achieve resistance to loss of bond at higher pH levels, and (d) it is possible to achieve a strong chemical bond between aggregate and asphalt cement that is resistant to pH shifts and a high pH environment. This strong chemical bond can be achieved by the formation of insoluble organic salts (such as calcium-based salts), which form rapidly and are not affected by high pH levels or pH shifts. Although pH shifts affect chemical bonds, it is important to keep the magnitude of the pH shifts in proper perspective. Normally a pH as high as 9 or 10 will not dislodge amines from the acidic surfaces of aggregates, nor will it affect hydrated lime. Values of pH greater than 10 are not normally developed in asphalt mixtures unless a caustic such as lime is added. However, pH below about 4 can dislodge amines from an aggregate surface and can dissolve lime, depending on the type of acid used; the lower pH is not found in hot mix asphalt (Little 2003).

The areas discussed and researched above were presented as theory. Actual research testing addressed adhesive failure versus cohesive failure, effect of aggregate characteristics, calculation of asphalt-aggregate bond strength, effect of asphalt composition on adhesion, effects of aggregate properties on adhesion, and SHRP research on aggregate surface chemistry. Ways to improve adhesion were studied in research papers addressing:

- interaction of acidic aggregates and asphalt with alkaline amine compounds.
- the effect of hydrated lime and other chemical treatments on adhesive bond.
- dusty and dirty aggregates and additional research studies on the general

mechanisms of bond disruption with dusty and dirty aggregates

- modification of dusty and dirty aggregates to improve asphalt-aggregate interaction.

The conclusions state that most asphalt pavements suffer moisture damage as a result of a combination of several processes. The shift in pH at the surface affects the ability to bond and causes the bonding to be dynamic over time. From a chemical standpoint, the literature is clear that neither asphalt nor aggregate has a net charge, but components of both have nonuniform charge distributions, and both behave as if they have charges that attract the opposite charge of the other material. Certain polar asphalt compounds combined with additives create the most durable, tenacious, and moisture-resistant bonds. From a physical standpoint the aggregate mineralogy, adsorbed cations on the aggregate surface, and surface texture and porosity affect the bond. Moisture damage is not limited to adhesion failure, but also a weakening of the mastic due to moisture infiltration. The weakening of the mastic due to water and its ability to absorb it might be a good case for thicker mastic cover on the aggregates (Little 2003).

Asphalt atoms are linked together to form molecules. Perhaps the simplest is the aliphatic carbon–carbon chain saturated with hydrogen bonds. The carbon–carbon bonds can also form rings saturated with hydrogen. These saturates are essentially nonpolar and interact primarily through relatively weak Van der Waals forces. A second class of asphalt molecules involves aromatics. This molecule has six carbon atoms in the form of a hexagonal ring. This ring possesses a unique bond with alternating single and double bonds between carbon atoms. Strong covalent bonds link atoms together to form asphalt molecules. These molecules interact with one another through much weaker bonds: pi–pi

bonds, hydrogen or polar bonds, and Van der Waals bonds (Jones 1992). Pi–pi bonds are unique to aromatic molecules. They provide polarity and the ability of aromatic molecules to link together in unique configurations, which includes a stacked arrangement. Heteroatoms among asphalt molecules develop polarity and link together by forming hydrogen bonds. A hydrogen bond is formed between two very important asphalt functional groups, a sulfoxide and a carboxylic acid. Van der Waals bonding is the weakest of the secondary bonds. It occurs when molecules cool or stress is removed. Van der Waals bonding is responsible for the free-flowing nature of asphalt at high temperatures versus the semisolid nature at lower temperatures (Jones 1992). As a point of reference, it is important to understand that covalent primary bonds within the molecule are from 10 to 100 times stronger than secondary bonds.

Polar molecules form “networks” through hydrogen and pi–pi bonds that give asphalt its elastic properties. Nonpolar materials form the body of the material in which the network is formed and contribute to the viscous properties of asphalt Jones, (1992). Degree of polarity is the most important property of polar molecules, while degree of aromaticity is the second most important. Highly polar and highly aromatic molecules form the most interactive and strongest molecular networks.

Effect of Aggregate Properties on Adhesion

A number of aggregate properties affect the adhesive bond between asphalt and aggregate including size and shape of aggregate, pore volume and size, surface area, chemical constituents at the surface, acidity and alkalinity, adsorption size surface density, and surface charge or polarity.

Hughes et al. (1960) and Scott (1978) reported that adhesion between asphalt

cement and aggregate in the presence of water became weakened when the pH of the buffer solution was increased from 7.0 to 9.0 (Scott 1978). Even granite, known to be acidic, showed an increase in pH over time to about 8.8. The granite reaction in water, which leads to this gradual pH increase, is, according to Yoon and Tarrer (1988), due to the silicate lattice reaction with the water to impart excess hydroxyl ions as follows:

$$-S-O-Na + H_2O \rightarrow -SiOH + Na+ + OH- \quad (1)$$

This is a typical hydrolytic reaction of the salt of a weak acid (Little 2003).

Yoon and Tarrer (1988) assessed the sensitivity of stripping to changes in pH of water in contact with the aggregate surface. The water susceptibility of the hydrogen bonds and salt links between the adsorbed asphalt components and the aggregate surface would increase as the pH of the water at the aggregate surface increases (Figure 1).

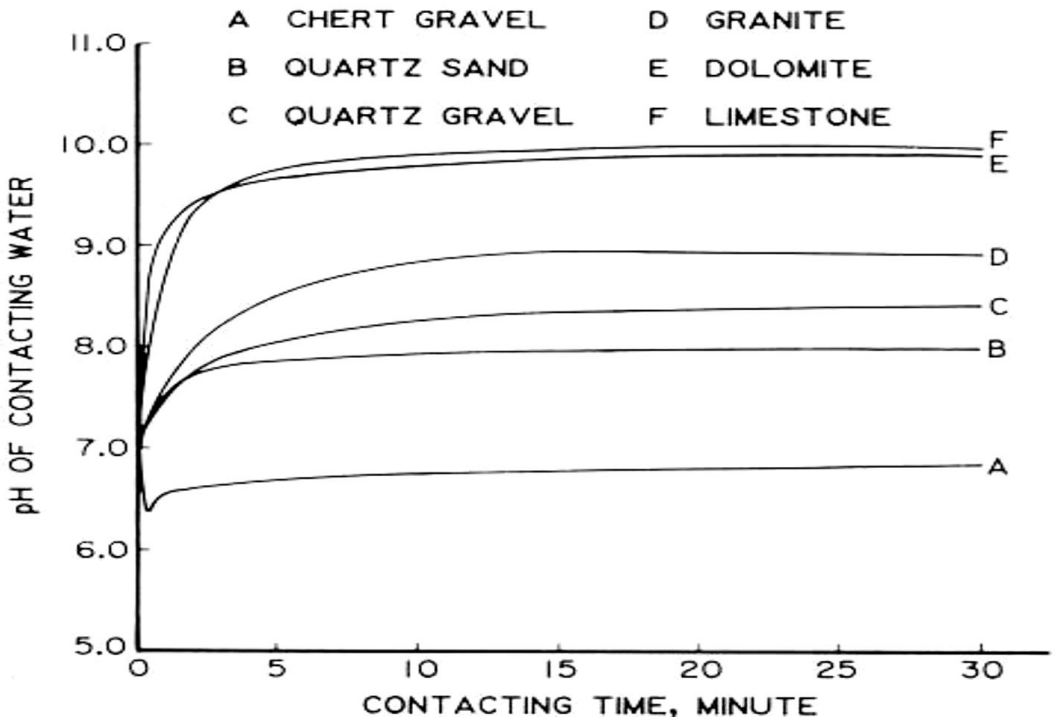

Figure 1 Changes in pH of Water in which Aggregates Were Immersed (After Yoon and Tarrer 1988.)

Therefore, it seems reasonable to conclude that stripping sensitivity will increase as the pH of the water increases. However, they warn that other surface aggregate properties also play a role. Different types of metal ions affect stripping potential. For example, alkaline earth metals in limestone associate strongly with the asphalt components in carboxylic acids to form alkaline earth salts, and the bonds formed are not dissociated easily in water even at a high pH. In other words, the adsorption is strong because of the insolubility of the alkaline earth salts formed between the limestone and the bitumen acids. Labib (1991) confirmed the existence of a range of acid–base types among various SHRP aggregates using zeta potential measurements and electrophoretic mobility. He reported that it is significant that the initial pH of aggregates was greater than 9.0, irrespective of aggregate type. This would neutralize the bitumen carboxylic acids at the interface and cause hydrolysis of bitumen–aggregate bonds. The high pH was attributed to basic soluble salts even in acidic aggregates. Labib (1991) documented the sensitivity of the bitumen–aggregate bond to pH. He identified three pH regions.

At pH above about 8.5 (Region 3), dissolution of the surface silica occurred in quartz or silica aggregates. In carbonate-based aggregates at pH between about 1 and 6 (Region 1), calcium ion dissolution occurred, and the presence of carboxylic acids enhanced stripping in this region through cohesive failure in the aggregate (Podoll 1991).

The SHRP adhesion model concludes that aggregate properties have a greater impact on adhesion than do various binder properties. Yoon and Tarrer (1988) discuss the effect of water pH on stripping potential in asphalt mixtures with respect to antistripping additives by comparing aggregate surface potential and stripping propensity using the boiling water tests (Figure 2).

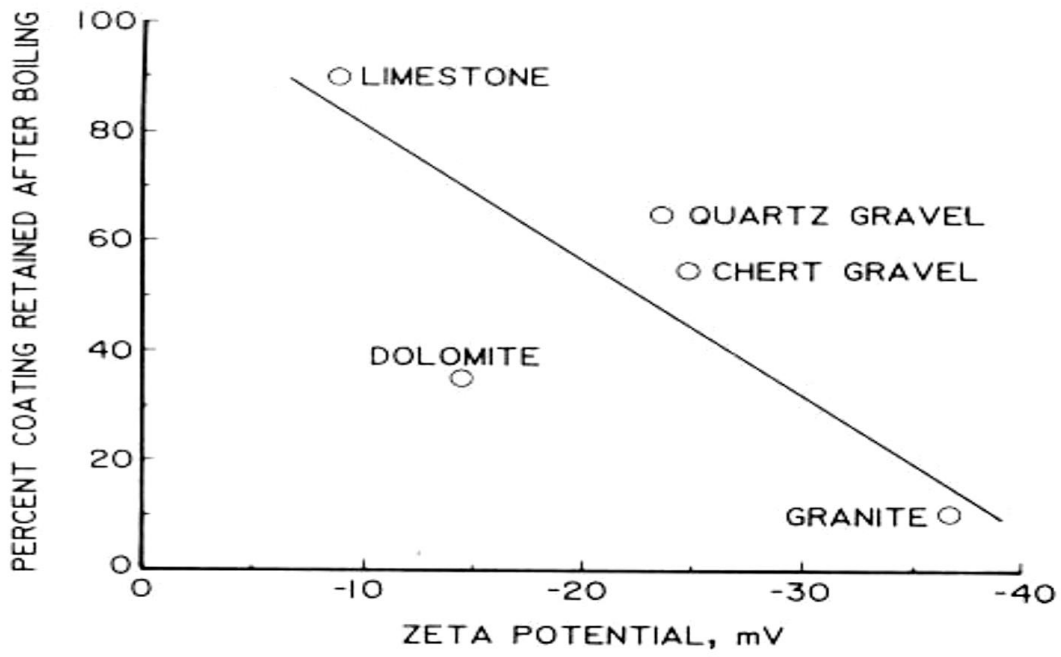

Figure 2 Comparison of Aggregate Surface Potential and Stripping Propensity as Determined by the Boiling Water Tests (After Yoon and Tarrer 1988.)

Their analysis showed that as the pH of the water increases, the adsorptive bonds between amine-type additives and aggregate surfaces are weakened. As a result, water can more easily displace asphalt from the aggregate surface. They point out that this is not the case with hydrated lime, where the resistance to stripping is independent of the pH of the contacting water. However, other research has shown that normally pH as high as 10 will not dislodge amines from the aggregate, and pH greater than 10 are very unusual. The asphalt–aggregate bond is affected by aggregate mineralogy, adsorbed cations on the aggregate surface, and the surface texture and porosity. Favorable chemical bonding between asphalt and aggregate alone will not optimize the adhesive bond and minimize moisture damage. The bond is part physical, and, therefore, the asphalt must be able to wet and permeate the aggregate surface. This process is dependent on asphalt rheology at mixing temperatures and the nature of the aggregate surface, pore size, pore

shape, and aggregate mineralogy. To complicate matters somewhat, the ability to bond asphalt to aggregate is dynamic and changes with time. This is largely affected by the shift in pH at the aggregate–water interface, which can be triggered by dissociation of aggregate minerals near the surface or by the nature of the pore water (cation type and concentration) (Little 2003).

In general, the tests that have been developed can be divided into two main categories: qualitative and quantitative. Qualitative tests provide a subjective evaluation of the stripping potential of loose asphalt mixes. The quantitative tests provide a value for a specific parameter, such as strength before and after conditioning, and are those tests for compacted mixtures (Solaimanian 2003). For a moisture susceptibility test procedure to be successful for mix design and field quality control, certain criteria must be satisfied:

1. It must be representative of the mechanisms that cause moisture damage in the field, and produce results that match those occurring in the field under similar conditions, or it must measure some property that determines the performance of the mix in the field without actually simulating field conditions in the laboratory.
2. It must be capable of discriminating between poor and good performers in regard to stripping. If the first criterion (above) cannot be satisfied, then some discriminator of this type is useful; however, the results must still be tied to field performance.
3. It must be repeatable and reproducible, with the allowable variance depending on the constraint of the fourth criterion.
4. It must be feasible, practical, and economical enough that it can be included in routine mix design practice.

The use of wheel tracking devices in the 1990s on asphalt mixes immersed in water has proven effective for determining if an HMA mix will pass or fail from a test inducing conditions to foster moisture damage. The Hamburg Wheel Tracker Device (HWTD) and the Asphalt Pavement Analyzer are testing equipment of this type. During the 1990s the environmental conditioning system was introduced, through the Strategic Highway Research Program (SHRP), to the industry. This occurred in 1993 at the completion of the SHRP research. Test procedures used to verify the stability of an asphalt mix to be used in paving a highway were improved with the research from the SHRP program. The development of the Hamburg Wheel Tracker Device allows testing of a Hot Mix Asphalt compacted specimen, and acceptance or rejection of the test depends on the amount of deformation caused by repeated loading over time. Although it is used in the asphalt industry primarily as a screening test for moisture sensitivity, the HWTD test has also shown promise in providing information on aggregate properties (Solaimanian and Kennedy 2000b).

Many variables in the field make field correlation difficult, but development of such a correlation remains absolutely necessary. This has been a major shortcoming in the development of effective laboratory tests that can provide quantitative results used in specifications and design across a wide range of conditions.

Correlation problems have existed in the Hamburg Wheel Tracker test data between interlaboratory test results, as well as the laboratory results and field observations. An important consideration of any test is calibration of the test to the conditions under which it will be applied. To address this variability, the Hamburg Wheel Tracker device needed to be successfully correlated between separate laboratories. Due to

a lack of correlation with field data, a lack of good field performance databases, and problems with the test variability and difficulty of operation, a series of interlaboratory study (ILS) tests were conducted by the Utah Department of Transportation (UDOT) to establish the reliability of the Hamburg Wheel Tracker Device used in Utah to determine the causes of failures of mixes in Utah. The results of these interlaboratory study tests are presented in a paper titled "On the Variability of Results from the Hamburg Wheel Tracker Device" (Cox 2013). The conclusions of this ILS and recommended procedures in preparation of the specimens for testing helped established uniformity and reliability in test results compared to any other laboratory test.

Mechanisms of moisture susceptibility/stripping may be different because of the different variables, but tests and their calibration must take into account materials, construction, traffic, and climate. The result will be that a given mix will have different risks, depending on where and how it will be used, and these factors must be accounted for in test development, test evaluation and calibration, and test implementation. Databases that include the required variables and sufficient numbers of projects do not exist at this time and are very difficult to develop. However, databases of this type are necessary for effective calibration of laboratory tests for moisture susceptibility and stripping (Solaimanian 2003).

With respect to the previous theories presented, the following theories and mechanisms of bitumen-aggregate adhesion were researched and addressed by Butt et al. (2003), Hicks (1991), Jamieson (1995), Kiggundu and Roberts (1988), Labib (1992), Little (2005), Little and Hefer (2005), Little and Jones (2003), Petersen et al. (1974), Rice (1958), Scott (1978), Tarrer (1992), Tarrer and Wagh (1990), Thelen (1958), Yoon and

Tarrer (1988). See the "A Summary of Theories and Mechanisms of Bitumen-Aggregate Adhesion" (Little 2005) (Appendix C**)**.

Additional Aggregate Research Findings

The following are basic rock chemistry. These findings will help in understanding the structure and chemistry of the rock. Minerals are composed of elements or groups of elements that unite in nature to form an inorganic crystalline solid. Every crystalline substance has a definite internal structure in which the atoms occur in specific proportions and are arranged in an orderly geometric pattern. This systematic arrangement of atoms is one of the most significant aspects of a mineral and exists throughout the entire specimen. Various ions can substitute for each other in the structure of some minerals. Several factors determine the suitability of one ion to substitute for another; the most important are the size and electrical charge of the ions in question (Hamblin & Howard 2005) (Figure 3).

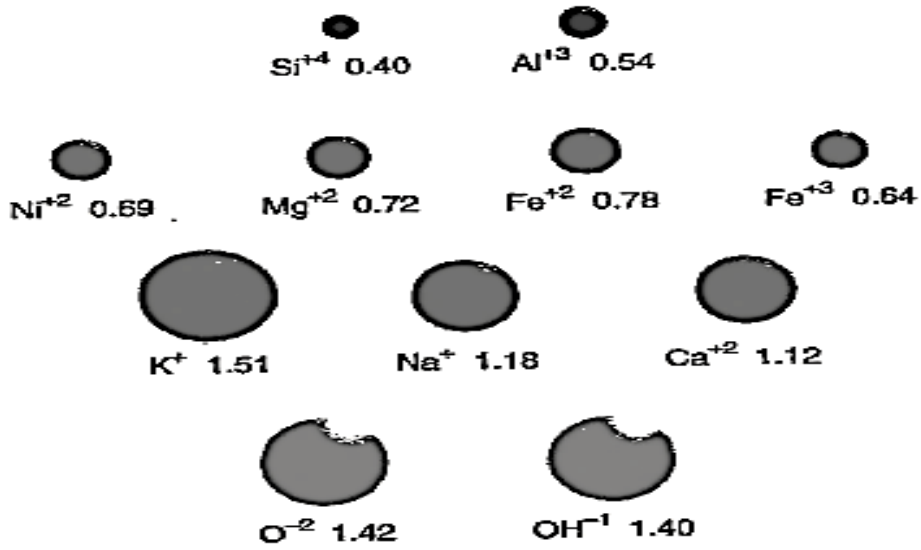

Figure 3 Relative Sizes and Electrical Charge of Ions (Hamblin & Howard 2005)

Mineralogical significance in igneous, sedimentary and metamorphic rock by texture and composition is as follows:

Igneous rock composition - Approximately 99% of the total bulk of most igneous rocks is made up of only eight elements or groups of elements.

Most of these elements occur in the crystal structure of the rock and form the silicate minerals of

- feldspars, olivines, pyroxenes, amphiboles, quartz and mica.
- These six minerals constitute over 95% of the volume of all common igneous rocks.

The texture is divided into the following types:

- phaneritic, porphyritic-phaneritic, aphanitic, porphyritic-aphanitic, glassy and pyroclastic (Table 2).

Table 2 Eight Most Abundant Elements of the Earth's Crust

Element	Percent in the earth's crust (by mass)	Symbol
Oxygen	**46.6%**	**(O)**
Silicon	**27.7%**	**(Si)**
Aluminum	**8.1%**	**(Al)**
Iron	**5.0%**	**(Fe)**
Calcium	**3.6%**	**(Ca)**
Sodium	**2.8%**	**(Na)**
Potassium	**2.6%**	**(K)**
Magnesium	**2.1%**	**(Mg)**

(Hamblin & Howard 2005)

Sedimentary processes produce a wide variety of rocks that differ in general appearance, but most sedimentary rocks fit into three major categories:

- clastic
- chemical
- organic.

Because sediment can come from any preexisting rock source, the composition of sedimentary rocks can be extremely variable and complex. Most sedimentary rocks are composed of materials that are abundant in other rocks and that are stable under the conditions of surface temperature and pressure. The great bulk of most sedimentary rocks are composed of only four constituents:

- quartz
- calcite
- clay minerals
- rock fragments.

Metamorphism of igneous and sedimentary rock due to recrystallization into a solid state without melting, changes the diagnostic features of the original rock by modification or obliteration. This occurs due to changes in temperature, pressure, and chemical composition of the fluids that flow through them. These restructured rocks are metamorphic rocks. The effects of metamorphism include

- Chemical recombination and the growth of new minerals, with or without the addition of new elements from circulating liquids and gases.
- Deformation and rotation of the constituent mineral grains.
- Recrystallization of minerals to form larger grains.

The net result is a rock of greater crystallinity, increased hardness, and new structural features that commonly exhibit the effects of flow or other expressions of deformation. All three major rock types can be metamorphosed, but intrusive igneous rocks and previously metamorphosed rocks are affected less by metamorphic processes than are the sedimentary rocks that are developed at Earth's surface (Hamblin & Howard 2005). The mineralogical significance of igneous, sedimentary, and metamorphic rocks is that they all trace back to the same eight elements for the bulk of their composition and texture. The composition and texture are determined by the percent of the major elements involved in their creation. Each rock is unique to its composition and can be changed or influenced by fluids, temperature, pressure and chemistry. These changes can affect the hardness and composition of the rock, as well as the percent of various elements within the rock.

Weathering Reactions

The first stage of the weathering process generally involves physical weathering processes that reduce the particle size of the material with no change in the chemical and mineralogical composition of the primary minerals. Physical weathering is very important since it creates greater surface area upon which chemical weathering can act. Chemical weathering involves processes that result in changes in the chemical and mineralogical structure of a primary or secondary mineral. Chemical weathering rates are regulated primarily by mineral surface area, temperature, leaching intensity (availability of water), mineral composition, proton flux, solution pH, and chelate concentration. Chemical weathering often includes the formation of new secondary minerals (i.e., clay minerals) that impart many important characteristics to the soil, such as ion exchange and

sorption capacity (Dahlgren 1996).

Mineral weathering rates are directly proportional to the mineral surface area exposed to weathering. Physical weathering processes are very important in breaking down the particle size of rocks, resulting in an increase in surface area. It is also believed that surface coatings of organic matter or iron oxides may block reactive mineral surfaces and may impede weathering rates because diffusion of reaction products and reactants is hindered by the surface coating (Dahlgren 1996). Primary minerals have widely varying stabilities to chemical weathering in the soil environment. For silicate minerals, the type of linkage between silica tetrahedral constituents is the primary factor affecting its stability. The greater the degree of Si-Si linkages, the more stable the mineral is toward chemical weathering. Minerals at the top of the diagram are dominant in basic igneous rocks (e.g., basalt) and are relatively unstable due to few Si-Si linkages in their mineral structure. The stability series of common soil minerals is as shown (Figure 4).

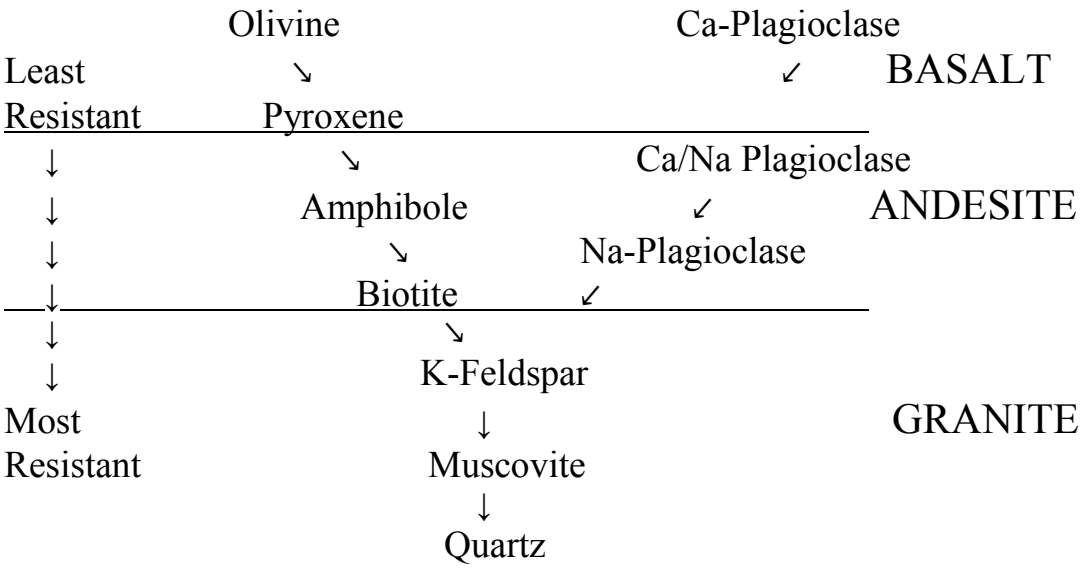

Figure 4 Stability Series of Common Soil Minerals (Dahlgren 1996)

The minerals toward the bottom of the diagram are common in acid igneous rocks (e.g., granite) and are relatively stable due to multiple Si-Si linkages in their structure.

As a result, minerals such as olivine quickly disappear with increased weathering while stable minerals such as quartz tend to accumulate. The solution pH and proton flux are important factors regulating reaction rates.

For most silicate minerals, dissolution rates show a minimum between pH 5 and 8 and increased rates above and below this range. This is due to the effect of H^+ and OH^- in forming surface active complexes with cations at the mineral surface that destabilize the internal cation bonds, resulting in release of the cation (Dahlgren 1996). It would appear that as the alkali hydroxide level in pore solution increases, (and therefore the pH), from cement alkalis or salt intrusions, the solubility of the aggregate silica increases (becomes available to form alkali-silica-hydroxide gels) (Tang 1980) (Figure 5).

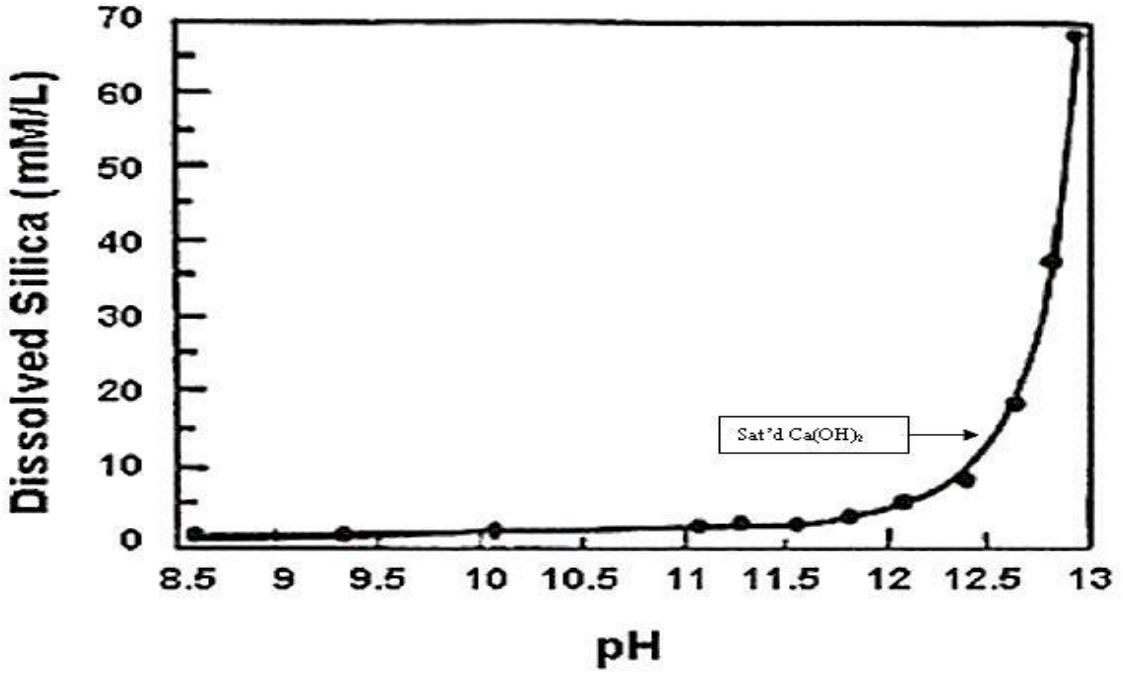

Figure 5 Effect of pH on Dissolution of Amorphous Silica (Tang 1980)

The pH of any one type of rock can vary dramatically as very few rocks could be called a “pure substance” due to the mechanism by which they were created. Another consideration is the permeability of the rock to liquids, which can solidify or crystallize within its structure. When rock is formed, or reformed, at high temperature or pressure, and are solid at normal temperature or pressure, can be made liquid. This will give various pH readings, dependent on how long the rock is allowed to sit in water.

CHAPTER III

METHODOLOGY

Source of Materials

Testing will be done using distilled water as the test medium. The pH value of the water used at the various HMA batch plants will be tested and recorded to eliminate batch plant water as a contributing source of high/low pH values.

Seventeen different contractor aggregate sources were located throughout the State of Utah. Two different asphalt binders, from asphalt binder sources approved by the UDOT asphalt testing laboratory, were obtained. Hydrated lime, as an additive, was obtained to evaluate its contribution to the pH of the HMA mixes.

The pH measurements were tested and recorded for the individual components: the two asphalt binder grades, the seventeen different aggregate sources, unboiled and boiled. Loose mix HMA specimens, including HMA mixes with and without hydrated lime added and with and without polyphosphoric acid formulated in the asphalt binders will be prepared, and the pH of the combined loose HMA mixes of the asphalt binder, and aggregates are to be recorded.

The following steps established the testing procedure to obtain the pH of the individual component and combined HMA mixes:

1. Record the pH value of the seventeen individual aggregate sources soaked in distilled water for 24 hours.

2. Record pH value of the individual water sources associated with existing HMA plants that use the aggregates from the seventeen sources.
3. Record pH value of the individual asphalt binders, with and without PPA.
4. Combine individual components into HMA mixes.
5. Record final pH value of HMA mix samples with and without lime added to the mix. These samples will be soaked for 24 hours in distilled water.
6. Statistically analyze the pH values and identify high- pH-contributing components.

The pH test values of these mixtures will be analyzed using a statistical program, which will determine the strength of the relationship between pH values and the contribution of each of the individual components comprising the loose HMA mixes with and without lime added. The samples with lime will be prepared at 1% lime added by weight. The aggregates from each pit will be assessed by the percent of mineral property shown by the chemical analysis of the pit aggregate (Appendix A) (Rigby 2010). The aggregate samples will be tested unmixed at 200-250 grams, by weight. HMA samples will be prepared and mixed at 150-250 gram, by weight, for testing. Asphalt binder will be added at 100 grams, by weight.

Procedure

The preparation procedure follows AASHTO T-182, which is used to prepare loose asphalt mixes. Individual components (Aggregate at 250-gram mass, Asphalt Binder-70-28 & 64-34 at 100-gram mass) were tested first and placed in containers and distilled water added to the same level in each container (300 milliliters). The samples were soaked for a 24-hour period and the pH reading taken and recorded. Mixtures of

aggregates, asphalt binder-70-28 & 64-34, with and without hydrated lime were mixed together to produce the individual loose HMA samples (HMA mix at 150-250-gram mass). When they cooled they were placed in containers and distilled water added to the same level in each container (300 milliliters). A calibrated pH meter (accuracy +/- 0.01%) was used to measure the pH test values. The same equipment was used to complete the preparation of the sample specimens (mixers, asphalt heating pots, drying ovens and certified scales) that are used to mix and verify hot mix asphalt designs submitted by contractors for use on the highways (Figures 6, 7, 8, 9 and 10).

Figure 6 pH Meter Used in Tests

Figure 7 Mixing Asphalt Samples

Figure 8 Mixed Sample of HMA

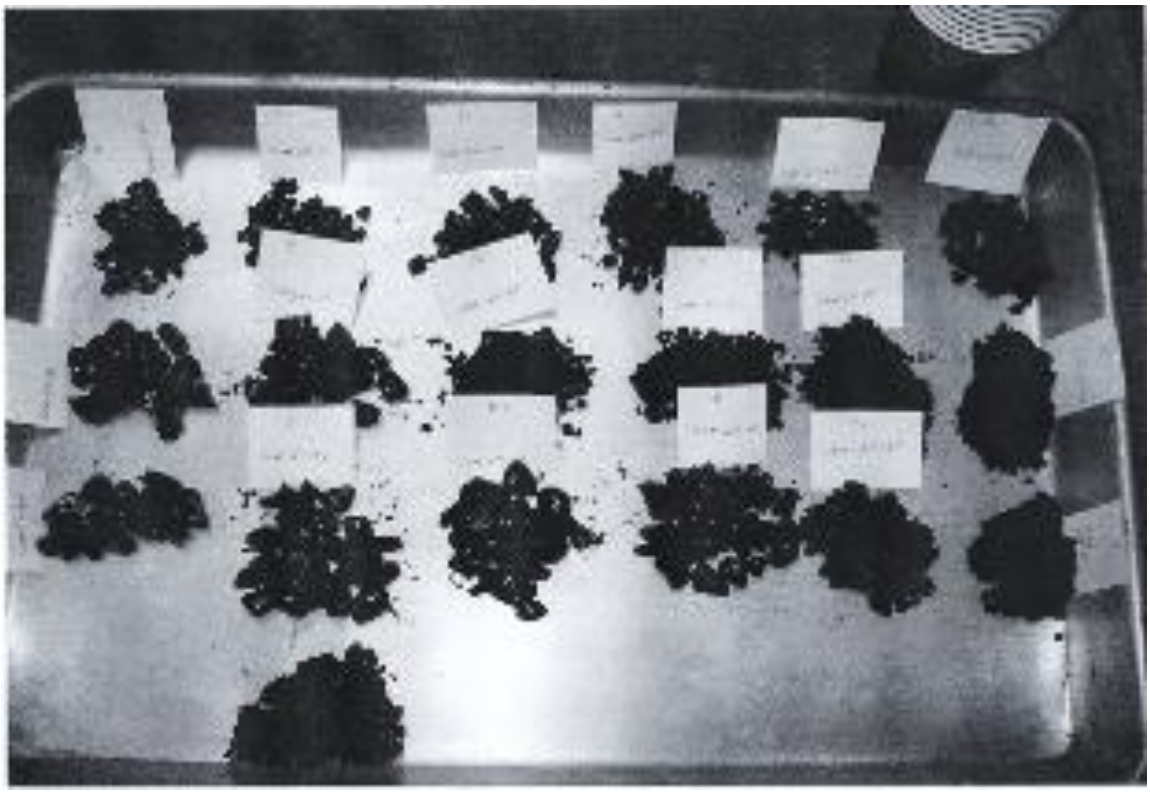

Figure 9 Mixed Samples from All Sources

Figure 10 Samples Immersed in Distilled Water

The recorded pH value of each component submerged in distilled water establishes a pH baseline of the individual components of the mix. The combined components were soaked 24 hours in 300 milliliters of distilled water, and the final pH of each sample was measured and recorded. An additional 24 hours of soaking time was allowed for 34 samples of mix 1-70-28 without lime and mix 1l-70-28 with lime samples to see if the pH value has remained the same or increased in value to determine if the testing period of 24 hours was sufficient time to allow infiltration of the water. A paired sample t-test will be done to see if the pH readings at 24 hours and 48 hours are actually different. The t value will determine if 24 hours of soaking was sufficient time for the mix to stabilize for an accurate pH reading. $H_{o:}$ pH mean values are equal. $H_{a:}$ pH mean values are not equal.

Chemical analysis data from a draft report to the Utah Department of Transportation on the mineralogical properties of course aggregate corresponded to the same sources used in this research. This work has provided UDOT with additional knowledge of how to improve pavement performance of Utah's roads. The results of the work provided the mineral percentages of the rock used in this study. This data, with permission of UDOT, has been incorporated to allow the interpretation of the pH results with the chemical analysis on the aggregate from the same source. Mineralogical properties of course aggregate from source pits 1, 2, 3, 4, 5, 6, 8, 9, 11, 12, 15, 16, and 17 were obtained from a draft report to UDOT (Rigby 2010). The results are presented in (Appendix A). Replicate pH readings of the same sample were not taken since the pH meter was calibrated and verified before each set of readings. The pH meter is accurate to +/- 0.01% and therefore any experimental error was deemed to be negligible.

Statistical Analysis of pH Data Using IBM SPSS - 21

To investigate the effects of various components on the pH of the HMA mix, a regression analysis method will be used with maximum likelihood estimation rather than linear discriminant analysis, since it is unlikely that the two methods will give markedly different results and the maximum likelihood method would be preferable where normality assumptions are violated when many of the independent variables are qualitative (Halperin et al. 1971). The purpose is to relate qualitative to explanatory variables. The approach taken involved first performing bivariate screenings of each component against HMA mix pH values, and then later combining all components found to be significant in the bivariate screenings into a multivariate regression model.

This type of model tests for a correlation between the dependent and independent variables or predictors. Since hydrated lime is used in all HMA mixes to enhance bonding, it is investigated to determine if its effects may be contributing to the chemical reaction of other components of the mix. Statistically there may be circumstances where hydrated lime contributes to the chemical reaction causing damage to the HMA mix:

$$\text{HMA mix pH} = \beta o + \beta_1 \text{Lime} + \beta_2 SiO_2 + \beta_3 CaO + \ldots\ldots\ldots\ldots + \beta_i \text{ etc.}$$

The null hypothesis is no significant relationship exists between the dependent HMA mix pH and any of the independent variables. Ho: All βs=0.

The research hypothesis (H_1) is there is at least one independent variable significantly related to HMA mix pH values. H_1: at least $\beta_i: \neq 0$.

Univariate Data Exploration was completed to determine the frequencies, and summary statistics and exploratory graphics are used for analysis. The categorical variables are analyzed by the frequency of observations within each level of a category.

The database contains the following categorical variables: pit location, oil (type), binder (source), hydrated lime at 1%, PPA, time, region, and a new category formula (percentages of minerals over 5 percent in each pit). Histogram plots of relative frequencies were run and analyzed for these categorical variables.

Descriptives of Continuous (Intervals) Variables

The continuous variables in this study were pH (the independent variable), phagg-boiled (related to the chemical characteristics of the aggregate), (SiO_2, $CaCO_3$, CaO, Al_2O_3, and MgO at the % above 5% shown in Appendix A). This establishes the central tendency of these variables, as well as what their distribution looks like. Reports of the mean and median along with standard deviation describe the spread. Histograms help understand the shape of the distribution of the responses.

To look for relationships or correlation and differences between pairs of the continuous variables, bivariate screening is used. This screening is to measure the strength of the linear relationship between the variables to see if there is a strong linear relationship between any of the continuous independent variables themselves. A strong linear relationship between the independent variables is undesirable, as it leads to problems with collinearity in the models.

Within bivariate screening, looking for relationships and differences between two continuous variables involves the computation of a Pearson correlation coefficient and/ or running of a simple linear regression.

Pearson Correlations tests use the following general form of the hypotheses being tested: The null hypothesis H_o: There is no significant linear relationship between a pair of variables and the alternative hypothesis H_a: There exists a significant linear

relationship between a pair of variables.

For measuring the strength of a linear relationship, the following guidelines (Salkind 2007) have been used regarding the absolute value of r:

- 0.7 or higher very strong
- 0.4 to 0.69 strong
- 0.3 to 0.39 moderate
- 0.2 to 0.29 weak
- 0 to 0.19 essentially no relationship

Independent variables with a high degree of correlation between them will not be used simultaneously in a regression model because the resulting collinearity causes instability in the model.

Chi-square Analysis

This is used to investigate whether the distribution of categorical variables differs from one another.

- H_o: There is not a significant relationship between the two variables.
- H_a: There is a statistically significant (dependent) relationship between the two variables.

The Chi-square test will be validated by running the Fisher Exact Test if too many cells have an expected count less than 5. This helps optimize the model.

One-way ANOVA tests are a very important part of the analysis, as they test whether or not there are significant relationships between continuous and categorical variables. Since the dependent variable, pH, is continuous, and many of the independent variables are categorical, these tests provide a way to screen the independent variables for

inclusion in a multivariate model. The hypothesis for the ANOVA test

- H_o: The mean pH is equal for both variables.
- H_a: The mean pH values for the two variables are significantly different.

Multivariate Model

Collinearity is when two independent variables are themselves so highly correlated that to put them both into the regression model would be redundant— that is, it would not really add any new information. When collinearity exists, the mathematics that actually solves the model becomes unstable, and the results cannot be trusted. The variance inflation factor (VIF) may be calculated for each predictor and is $1/ (1-R^2)$. This estimates how much the variance of a coefficient is inflated because of linear dependence with other predictors. A VIF of 1.38 would mean that the variance of a particular coefficient would be 38% larger than it would be if that predictor was completely uncorrelated with the other predictors. This analysis is done to keep the model stable. An example is a correlation between the continuous variables in the potential model as follows: The ones in this model would be SiO_2, $CaCO_3$, and CaO. With these three variables in the model simultaneously, the variation inflation factor (VIF) is too high, > 10, and they all cannot be justified in the model based on p-value. The highest p-value is removed and correlation rerun until the VIF is less than 10 and the p-value is less than 0.05 for the remaining variables. For example, a potential model with only SiO_2 and CaO would be significant if both have a p-value of less than 0.05.

The main effects model is used to establish that the independent variable is correlated with the dependent variable. This model will be run to determine which variables might have a significant correlation with the outcome variable— for example,

Hydrated lime, SiO_2, and CaO, etc.

Assessing the Strength of the Model

The Shapiro-Wilks test will be used to assess whether or not the residuals are normally distributed. A normal curve provides the basis for the probability associated with a possible outcome and to determine the degree of confidence that a particular finding is true.

After the model is optimized it will be rerun, with the residual plots checked for fit.

- H_o: The model is normally distributed and a 'good' fit.
- H_a: The model is not normally distributed and a 'poor' fit to the data.

CHAPTER IV

RESULTS

All recorded data results were analyzed statistically for comparison purposes. This included data with hydrated lime added and data without hydrated lime added. The following Univariate Data Exploration follows the outline presented in the methodology chapter.

Frequencies

Frequencies were run for all the categorical variables. The frequency for each pit or source shows 14 samples from each pit or source with and without lime and shows seven samples from each pit or source without lime. These results would indicate the data for this variable are reasonably balanced.

The frequency for the oil or supplier shows 102 samples from each supplier read at 24 hours and the other 34 samples pH values read at 48 hours, using only one of the suppliers for soaking time verification. The data for this variable are evenly balanced.

The binder or grade has an approximate 70% - 30% distribution because the 64-34 grade was not formulated with PPA. Therefore, additional pH values were taken with the 70-28 grade which contained PPA for both the analysis of samples with lime and without lime.

The hydrated lime frequency shows 119 tests with hydrated lime and 119 tests

without hydrated lime. This indicates the data for this variable are reasonably balanced.

The PPA frequency plot is the same as the binder or grade, since the 64-34 grade was not formulated with PPA and has the same 70% - 30% distribution.

The time or hours frequency plot has an 86%-14% distribution, since the 48-hour pH readings were taken on 34 samples only to compare to the 24 hour soaking period to determine adequate soaking time, as explained in the methodology chapter. The same is true for the samples with and without lime.

The region is determined by population and location of the source or pits. UDOT Regions 1 and 2 include the north pits, and UDOT Regions 3 and 4 include the south pits. The frequency plot distribution is 59% north and 41% south because there are more pits in the north. This remains true for samples with and without lime.

The formula category represents the mineralogy or chemistry of the various sources or pits. The category has twelve possible formulations (Appendix A) (Rigby 2010). The formulas were obtained by chemical analysis of the aggregate from the source or pit. Formula nine appeared more often than the other formulas, as most contractor sources or pits have similar chemistry for meeting required aggregate specifications (Figure 11).

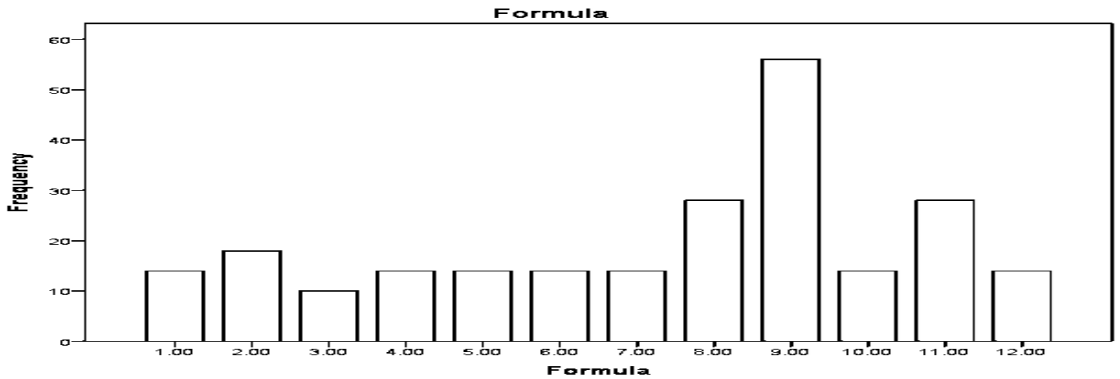

Figure 11 Frequency Plotted against 12 Locations Chemical Analysis Formulas %

Those most frequently used formulas were from pits or locations whose aggregate chemistry was the same. Only the chemistry components with percentages higher than 5% were included in the analysis, as the smaller percentages were considered minor contributors to chemical reaction. This remains true for samples with and without lime.

Descriptives of Continuous (Intervals) Variables

The HMA mix pH histogram plots, with and without lime, are superimposed with bell curves on them and are included for information as they bring the data into subgroups for discussion purposes (Figures 12 and 13).

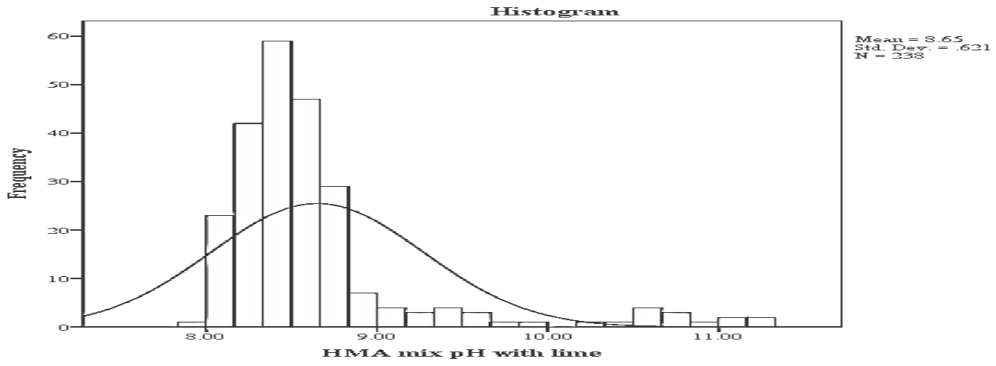

Figure 12 Histogram and Mean of HMA Mix pH with Lime

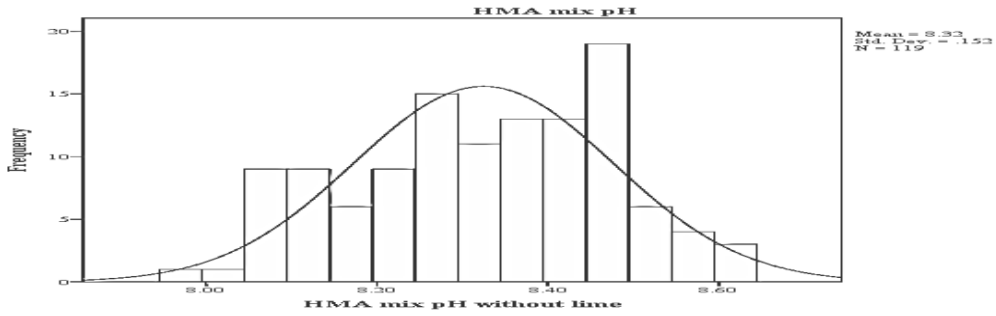

Figure 13 Histogram and Mean of HMA Mix pH without Lime

The histogram plot of HMA mix pH with lime is skewed to the right and the plot without lime is a more uniform normal distribution.

The mean for HMA mix pH with lime is 8.65, whereas the median is 8.495. This median is much closer to the mean and median of the HMA mix pH without lime at 8.32 and 8.34, respectively. When a highly skewed variable, such as HMA mix pH (2.506), is observed, the median should be used more than the mean to describe its central tendency. Identifying the reason for the high pH is the focus of the remaining discussion and emphasis of the dissertation. Continuous variables in this study were pH (the dependent variable), phagg-boiled (related to the chemical characteristics of the aggregate), SiO2, CaCO3, CaO, Al2O3, and MgO or formula expressed as percentages of the chemical analysis of the rock. Output of summary statistics shown (Tables 3 and 4).

Table 3 Output Summary Statistics: Continuous Variables with Lime

	N Statistic	Minimum Statistic	Maximum Statistic	Mean Statistic	Std. Deviation Statistic	Skewness Statistic
HMA mix pH	238	7.97	11.30	8.6508	.62114	2.506
SiO_2	238	.20	.82	.6018	.19335	-.692
$CaCO_3$	238	.05	.80	.2093	.21143	1.612
CaO	238	.00	.34	.1044	.08931	1.416
Al_2O_3	238	.00	.15	.0608	.03194	1.190
MgO	238	.00	.15	.0487	.05105	.849
Valid N(listwise)	238					

Table 4 Output Summary Statistics: Continuous Variables without Lime

	N Statistic	Minimum Statistic	Maximum Statistic	Mean Statistic	Std. Deviation Statistic	Skewness Statistic
HMA mix pH	119	7.97	8.61	8.3247	.15215	-.221
SiO_2	119	.20	.82	.6018	.19376	-.696
$CaCO_3$	119	.05	.80	.2093	.21187	1.622
CaO	119	.00	.34	.1044	.08950	1.425
Al_2O_3	119	.00	.15	.0608	.03201	1.197
MgO	119	.00	.15	.0487	.05115	.855
Valid N(listwise)						

Observations from the descriptive continuous variables with lime are

- A skew that has an absolute value greater than one is regarded as significant. An incredibly high positive skew is the dependent variable HMA mix pH (2.506). Because of the extreme skew, the median more than the mean will be used to describe central tendency,
- This is problematic because regression work is best when the dependent variable has a normal distribution.
- From observation quite a few pH values were above the mean, suggesting more investigation as to reasons or cause for the skew may be necessary.

Observations from the descriptive continuous variables without lime are:

- No right-tailed skew for the pH less than 1, but right-tailed skews remain for the $CaCO_3$, CaO, and Al_20_3 continuous variables, which is regarded as significant.
- A model for the dependent variable HMA mix pH should be more reliable since the underlying assumption of normality appears to be met.
- It should be noted that addition of lime accounted for ALL of the samples for which pH exceeded 9. This appears to be a primary factor affecting the pH of the final mix (Figure 14).

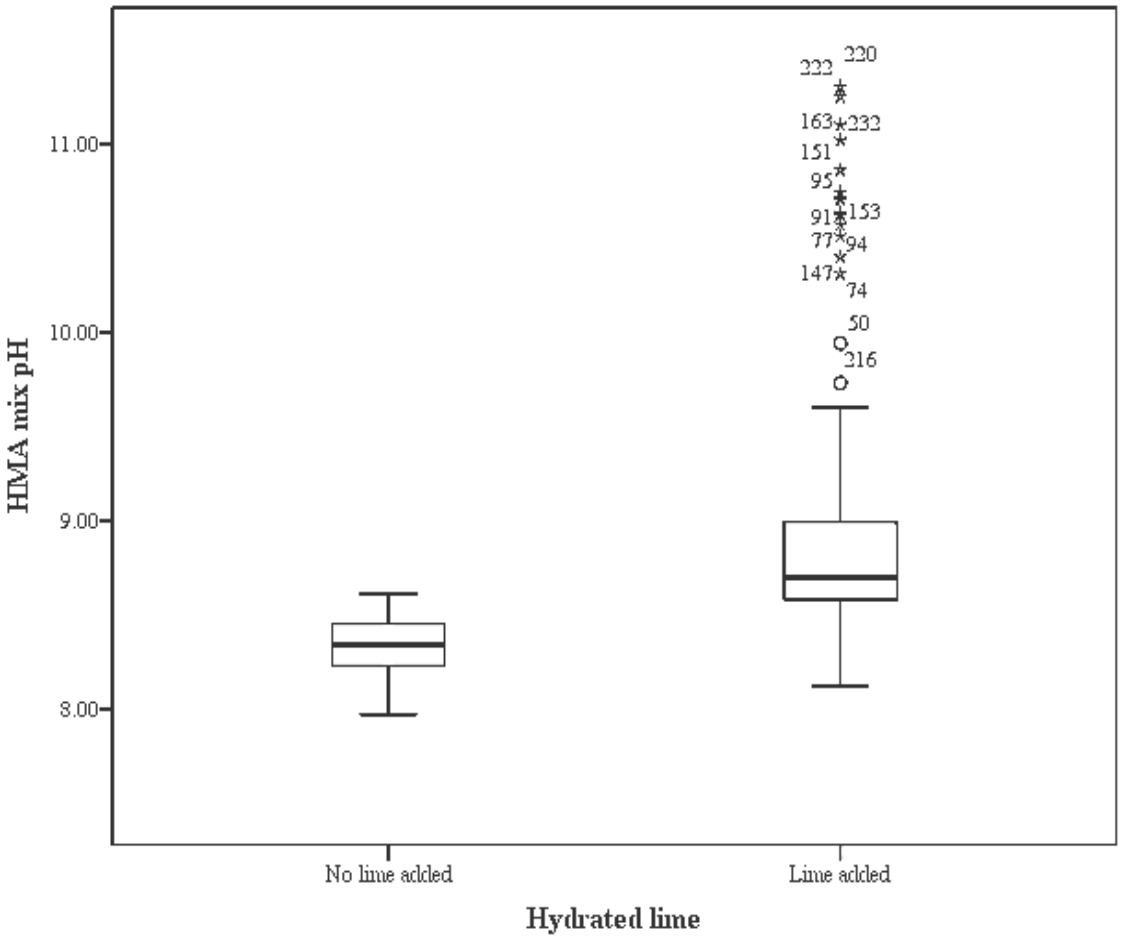

Figure 14 Comparison Plot of HMA Mix pH with and without Hydrated Lime

The comparison of the locations, pit or sources, with and without hydrated lime added, point to four locations, pit or sources which have pH readings significantly different when the lime is present. Pits 13 and 16 have pH readings with lime averaging near 9.4, but drop to 8.15 without lime added. Pits 14 and 17 have pH readings with lime near 8.60, but drop to 8.45 without lime added, resulting in a 13% decrease and a 2% decrease in pH, respectively. The chemistry of pit 13 is mainly limestone, and pit 16 is 48% SiO_2, 13% $CaCO_3$ and 12% Al_2O_3. Pit 14 is 59% SiO_2, 15% CaO, and 15% MgO, and pit 17 is 49% SiO_2, 10% $CaCO_3$, and 15% Al_2O_3. The remaining locations or pits vary approximately 2% with or without hydrated lime added. It should be noted the aggregate chemistry at these locations, coupled with lime, seems to be creating higher pH mean values. The mean plots of HMA mix versus location pit or source are shown (Figures 15 and 16).

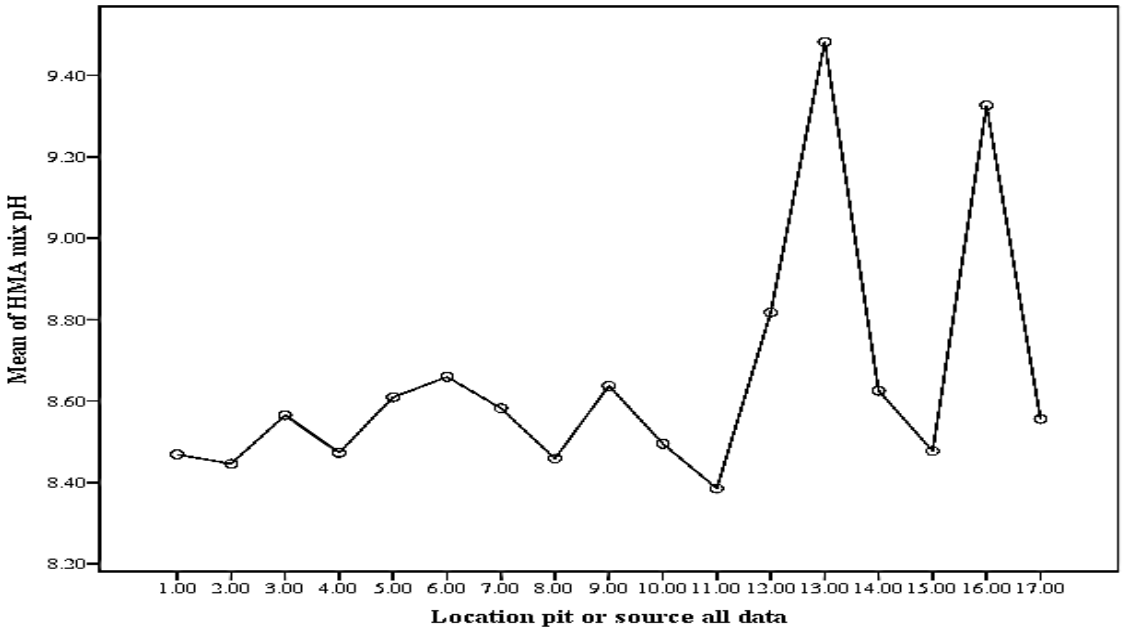

Figure 15 Mean Plot of HMA Mix all Data vs Location Pit or Source

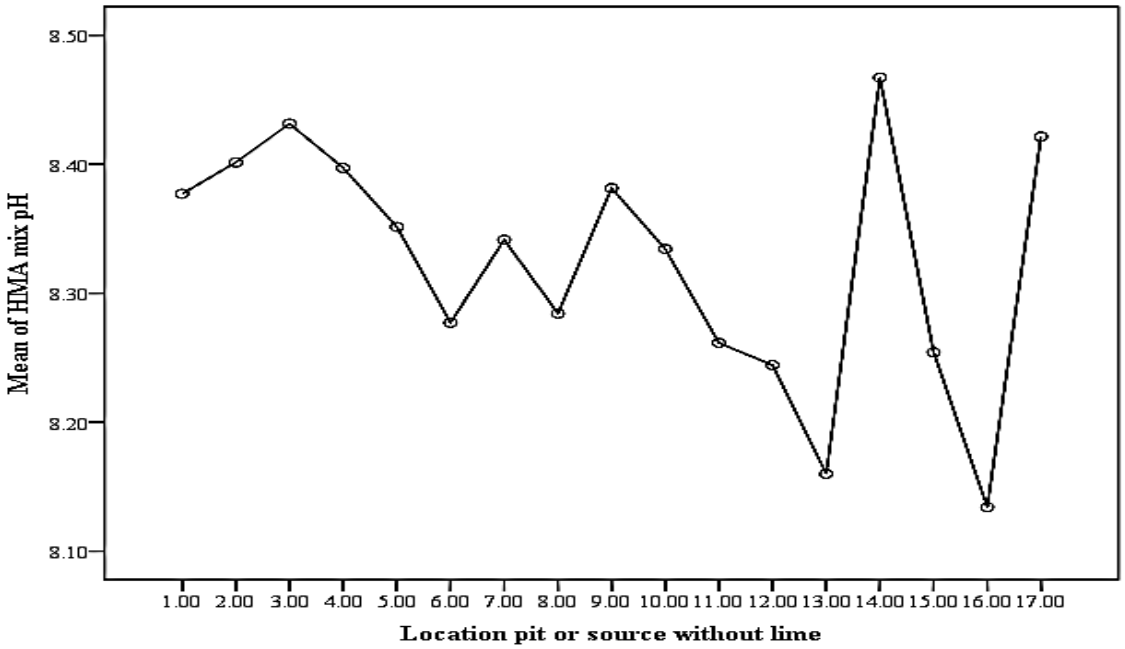

Figure 16 Mean Plot of HMA Mix without Lime vs Location Pit or Source

Further statistical testing will be done to analyzed and verify this condition.

Bivariate Screening

Bivariate screening was completed to further investigate and establish any correlation between any other pairs of the independent variables.

The independent variables found to be significantly correlated with HMA mix pH (at a 0.05 significance level) were

- SiO_2, r = - .203, p = 0.002
- $CaCO_3$, r = .182, p = 0.005
- CaO, r = - .175, p = 0.007

According to the strength guidelines, with Pearson correlations at .20 or less, the relationship is a very weak one and is even negligible. All these had a p-value of less than .20 in the bivariate screening. The strongest relationship among the independent variables

is between SiO_2 and $CaCO_3$. With a Pearson correlation coefficient of – 0.854, this indicates that as SiO_2 increases, $CaCO_3$ decreases. They are too highly correlated to both be present in a regression analysis, so a variance inflation factor, VIF, will be computed to see if collinearity is a problem. CaO is strongly correlated with SiO_2, r = - .514, p = 0.000. As an important part of this analysis, one-way ANOVA tests were completed on all variables to determine whether or not there are significant relationships between continuous and categorical variables. This will screen independent variables for possible inclusion in the multivariate model. The screening resulted in the following P-values, which were used in selecting the independent variable to include in the final multivariate regression model (Table 5).

Table 5 Results of Bivariate Screening of Independent Variables, against pH with Lime

Variable	Type	F-statistic	P-value	Comments
pit	Categorical	4.005	0.000	Include
Oil	Categorical	0.215	0.643	Do not include
Binder	Categorical	2.324	0.129	Include
Lime	Categorical	90.294	0.000	Include
PPA	Categorical	0.039	0.843	Do not include
time	Categorical	1.310	0.253	Do not include
region	Categorical	11.415	0.001	Include
SiO2	Continuous	6.996	0.000	Include
CaCO3	Continuous	3.680	0.000	Include
CaO	Continuous	5.740	0.000	Include
Al2O3	Continuous	5.740	0.000	Include
MgO	Continuous	5.740	0.000	Include

Bivariate comparisons were made between all pairs of categorical variables in order to check for independence.

Pearson Chi-square tests of independence are used to investigate whether distributions of categorical variables differ from one another. The eight categorical variables are pit, oil, binder, lime, PPA, time, region, and formula. All the variables with a p-value of 0 are not independent of each other. Those variable pairs found not to be independent were pit/region, pit/formula, oil/time, binder/PPA, etc. These were identified so as to ensure that in multivariate regression work, no two highly dependent variables would be considered in a regression model simultaneously. These variables are bolded **0** (Table 6).

Table 6 Results of Bivariate Screening of Independent Variables, against pH without Lime

Variable	Type	F-statistic	P-value	Comments
pit	Categorical	3.644	0.000	Include
Oil	Categorical	6.255	0.014	Include
Binder	Categorical	6.078	0.015	Include
PPA	Categorical	0.556	0.458	Do not include
time	Categorical	22.000	0.000	Include
region	Categorical	8.51	0.004	Include
SiO2	Continuous	6.996	0.000	Include
CaCO3	Continuous	3.680	0.000	Include
CaO	Continuous	5.740	0.000	Include
Al2O3	Continuous	5.740	0.000	Include
MgO	Continuous	5.740	0.000	Include

Even though from the Pearson Chi-square tests there was no need to run the Fisher exact test to make conclusions, the Fisher exact test was run on the data for lime added and no lime added, to examine the data and to thoroughly understand any differences present within the data so as to understand how variables may function together as independent variables in a statistical model. The results were that certain pairs of variables, such as pit/binder, are structured to ensure independence.

After running the Fisher test there are two situations happening that have caused violation of the conditions under which a Chi-square test of independence are appropriate: 1- Those situations where the two variables are completely confounded (p-value = 0), and both variables are never used in a model simultaneously, and 2- Those situations where the design of the experiment has been set up so that the variables are independent and therefore there is no problem considering both simultaneously. In neither of these cases does Fisher's exact test give any additional information. Fisher's exact test confirmed the results of the Chi-square results and verified the use of the chosen variables for the model.

The mean pH levels were looked at across all the pits to see if they were the same. This was completed for pits with lime and without lime. Without lime the mean was 8.32 and with lime the mean was 8.98. Pits 13 and 16 (with lime) show pH values of 10.8 and 10.51 as mean values. The Levene's test shows not equal variances exist, since pit 3 had a standard deviation of .07, while pit 16 had a 0.73, ten times as great. It is significant how high the mean pH values are from pits 13 and 16. A significant difference in the mean pH value for the different pits was detected, $F(16,221)$, $p = 0.000$. The tables show results for all pits using all the data, with and without lime added (Table 7, 8, 9 and 10).

Table 7 Chi-Square Tests of Independence

Categories	Chi-square	df	p-value
pit, oil	0	16	1
pit, binder	0	16	1
pit, lime	0	16	1
pit, PPA	0	16	1
pit, Time	0	16	1
pit, region	238	16	**0**
pit, formula	2618	176	**0**
oil, binder	1.983	1	0.159
oil, lime	0	1	1
oil, PPA	1.983	1	0.159
oil, Time	29.75	1	**0**
oil, region,	0	1	1
oil, formula	0	11	1
binder, lime	0	1	1
binder, PPA	38.08	1	**0**
binder, Time	15.867	1	**0**
binder, region	.000	1	1
binder, formula	.000	11	1
lime, PPA	.000	1	1
lime, Time	.000	1	1
lime, region	.000	1	1
lime, formula	.000	11	1
PPA, Time	15.867	1	**0**
PPA, region	.000	1	1
PPA, formula	.000	11	1
Time, region	.000	1	1
Time, formula	.000	11	1
region, formula	209.100	11	**0**

Table 8 Anova HMA Mix pH all Data

HMA mix pH

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	20.555	16	1.285	4.005	.000
Within Groups	70.884	221	.321		
Total	91.439	237			

Table 9 Anova HMA Mix pH with Lime

HMA mix pH

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	50.710	16	3.169	25.466	.000
Within Groups	12.694	102	.124		
Total	63.404	118			

Table 10 Anova HMA Mix pH without Lime

HMA mix pH

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.994	16	.062	3.644	.000
Within Groups	1.738	102	.017		
Total	2.732	118			

The results for all pits using only the data with lime added show a substantial difference in the mean pH value for the different pits F (16, 102), p = 0.000. The results for all pits using only data without lime added also show a substantial difference in the mean pH value for the different pits F (16,102), p = 0.000.

A t-value for the paired samples of the pH of the 24-hour soaking period versus the 48-hour soaking period was computed. The p value of the correlations was p = 0.000. If the obtained value is more extreme than the critical value, the null hypothesis cannot be accepted. If the obtained value does not exceed the critical value, the null hypothesis is the best explanation.

The t value needed for rejection of the null hypothesis at df = 33, 0.05 two-tailed test is 2.03 from Table B-2 (Salkind 2007). Therefore, null hypothesis cannot be rejected and the 24-hour soaking period is adequate. The statistical results are shown (Table 11).

Table 11 Paired Samples Test Results

Pair	Mean	Std. Deviation	t	df	Sig. or p-value(2-tailed)
pH-pH	-.04735	.21343	-1.294	33	.205

Multivariate Model

As the research question contains more than one variable, multivariate analysis of variance, which looks at group differences but controls the relationship between the independent variables, will be used to evaluate the objectives of this study.

As a starting point to multiple regressions, all variables that had a p-value less than 0.15 in the bivariate screening against pH were included. Finally, all variables found to be significant at an alpha of 0.05 were retained.

Using the General Linear Model, analyses were run with lime, with the following results:

- From the Main Effect's Model, it was determined that CaO, (with p-value of 0.64, could be dropped), leaving hydrated lime and SiO_2 as variables to be used in the model as all others were statistically eliminated.
- Hydrated Lime - F = 123.93, p = 0.000 and SiO_2 - F = 10.77, p = 0.000.

From this analysis, it is noted earlier that addition of lime accounted for ALL of the samples for which pH exceeded 9. This appears to be a primary factor affecting the pH of the final mix.

Note that all variables that remain in the model are significant, with p-values all reported as 0.000.

Using the general linear model, analyses were run on data without lime, with the

following results:

- From the Main effect's model for data without lime it was determined that $CaCO_3$ was redundant and SiO_2 was significant, so SiO_2 was used in the model as all others were statistically eliminated.
- SiO_2 - F = 4.454, p = 0.000.

Assessing the Strength of the Model with Lime

The Shapiro-Wilks test, to assess whether or not the residuals are normally distributed, will be used to check the residuals. This test detects departures from normality due to skewness or kurtosis or both.

The plot of predicted versus observed values was scattered and not lined up in a straight line and does not look good for fit. The model is not good for making predictions or inferences F (9, 218) = 41.176, p = 0.000.

Assessing the Strength of the Model without Hydrated Lime

The plot of predicted versus observed values was also scattered and not lined up in a straight line and does not look good for fit. The dots present in the output table meant the test was unable to run, as the algorithm broke down. Nothing can be taken from this model.

The tests between-subject's effects result in a value of .493(Adjusted R Squared = .471). This R value indicates that this model explains 47- 49 % of the observed variation in final pH levels. As the testing data was analyzed it reduced the variables down to two significant contributors as show in the tables. Tests between-subjects' effects and parameters with lime were run and the results are shown (Tables 12 and 13).

Table 12 Tests pH of Between-Subjects Effects with Lime

Dependent Variable: pH of HMA mix with lime

Source	Type III Sum of Squares	df	Mean Square	F	Sig.	Partial Eta Squared	Noncent Parameter	Observed Power[b]
Corrected Mdl	45.091[a]	10	4.509	22.084	.00	.493	220.841	1.000
Intercept	14024.77	1	14024.77	68689.06	.00	.997	68689.06	1.000
Lime	25.303	1	25.303	123.929	.00	.353	123.929	1.000
SiO2	19.787	9	2.199	10.768	.00	.299	96.912	1.000
Error	46.348	227	.204					
Total	17902.36	238						
Corrected Tot.	91.439	237						

a. R Squared = .493 (Adjusted R Squared = .471)
b. Computed using alpha = .05

Table 13 Parameter Estimates with Lime

Dependent Variable: pH of HMA mix with lime

Parameter	B	Std. Error	t	Sig.	95% Confidence Interval		Partial Eta Sqrd	Noncent Parameter	Obsd Power[b]
					Lwr Bnd	Upr Bnd			
Intercept	8.892	.076	117.576	.000	8.743	9.041	.984	117.576	1.000
[Lime=.00]	-.652	.059	-11.132	.000	-.768	-.537	.353	11.132	1.000
[Lime=1.00]	0[a]	.	.	.	.	.	.	.	.
[SiO2=.20]	.916	.139	6.572	.000	.642	1.191	.160	6.572	1.000
[SiO2=.31]	-.093	.110	-.842	.401	-.310	.124	.003	.842	.134
[SiO2=.40]	-.071	.139	-.507	.613	-.345	.204	.001	.507	.080
[SiO2=.48]	.761	.139	5.455	.000	.486	1.035	.116	5.455	1.000
[SiO2=.49]	-.010	.139	-.072	.943	-.285	.265	.000	.072	.051
[SiO2=.59]	.059	.139	.425	.671	-.215	.334	.001	.425	.071
[SiO2=.68]	.162	.110	1.468	.144	-.055	.379	.009	1.468	.309
[SiO2=.72]	-.042	.092	-.452	.651	-.223	.140	.001	.452	.074
[SiO2=.75]	-.181	.139	-1.296	.196	-.455	.094	.007	1.296	.252
[SiO2=.82]	0[a]	.	.	.	.	.	.	.	.

a. This parameter is set to zero because it is redundant.
b. Computed using alpha = .05

From parameter estimates, when SiO_2 is held constant at 20 % on average there is a decrease in pH of 0.652 units.

The 95% confidence interval for this decrease is 0.537, 0.768. When controlling for the addition of lime, SiO_2 = .20 or 20% is associated with a .916 increase in pH. The 95% confidence interval for this increase is 1.191, 0.642 and SiO_2 =.48 or 48% is associated with a .761 increase in pH. The 95% confidence interval for this increase is (1.035, 0.486). The tests between subject's effects result in a value of .269, (Adjusted R Squared = 0.209).

The above tests lead to mathematical models.

This R value indicates that this model explains 20- 27 % of the observed variation in pH levels (Tables 14 and 15).

Table 14 Tests pH of Between-Subjects Effects without Lime

Dependent Variable: HMA mix without lime

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	.735[a]	9	.082	4.454	.000
Intercept	6377.533	1	6377.533	348055.974	.000
SiO2	.735	9	.082	4.454	.000
Error	1.997	109	.018		
Total	8249.518	119			
Corrected Total	2.732	118			

a. R Squared = .269 (Adjusted R Squared = .209)
b. Computed using alpha = .05

Table 15 Parameter Estimates without Lime

Dependent Variable: HMA mix without lime

Parameter	B	Std. Error	t	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Intercept	8.369	.030	283.308	.000	8.310	8.427
[SiO2=.20]	-.209	.059	-3.530	.001	-.326	-.091
[SiO2=.31]	-.053	.047	-1.132	.260	-.145	.040
[SiO2=.40]	-.034	.059	-.580	.563	-.151	.083
[SiO2=.48]	-.234	.059	-3.966	.000	-.351	-.117
[SiO2=.49]	.053	.059	.895	.373	-.064	.170
[SiO2=.59]	.099	.059	1.669	.098	-.019	.216
[SiO2=.68]	-.056	.047	-1.193	.235	-.148	.037
[SiO2=.72]	-.024	.039	-.612	.542	-.101	.054
[SiO2=.75]	-.107	.059	-1.814	.072	-.224	.010
[SiO2=.82]	0[a]	.	.	.	.	.

a. This parameter is set to zero because it is redundant.
b. Computed using alpha = .05

Through a manual optimization procedure, a statistically significant model was developed for relating pH to two and one independent variables.

Mathematically the models take the form:

$$pH = 8.892 - 0.652\ (Lime) + 0.916\ (SiO_2) \quad (2)$$

$$pH = 8.369 + .099\ (SiO_2) \text{ at } .59 \text{ or } 59\% \text{ (without lime)} \quad (3)$$

SiO_2 is a continuous variable, whose value ranged between 0.2 or 20%, 0.82 or 82% as used in this research study. No attempt should be made to extrapolate outside of these ranges. Lime assumes a value of 1 when it has been added to the mix and 0 otherwise. The model is assessed as being poorly fitting, but from R Squared = .493 (Adjusted R Squared = .471), explains approximately 47-49 % of the pH variation, and caution should be used for prediction purposes.

The biggest determinant of whether or not pH will exceed a value 9.0 pH appears

to be whether or not hydrated lime is added. Among the 238 samples examined in this analysis, there were no instances where lime was not added in which the mix exhibited high pH values.

The results point to aggregate chemistry to explain pH values between 8.495 pH, the median of this study with lime and 9.0 pH, the value at which every pH above it had lime added. This is significant in some locations or sources when adding lime, as together they may enhance the chance for moisture damage affecting adhesion. Aggregate properties have a greater impact on pH values than do various asphalt binder formulations. Type of oil showed 70-28 was not significant, but 64-34 was on the border of having 95 % confidence.

CHAPTER V

SUMMARY OF RESULTS, CONCLUSIONS AND RECOMMENDATIONS

Summary of Results

The research scale was large, with many categorical and continuous variables. To successfully analyze the data with any degree of accuracy required assessing the output of the statistical data to eliminate collinearity and redundancy of the variables. Many of the categorical variables were, at inception, set up to be independent. The categorical and continuous variables were either dependent, independent, or confounded by the analysis, resulting in statistical elimination of most of them.

A paired sample t-test validated that the pH readings at 24 hours and 48 hours are the same. The null hypothesis could not be rejected $H_{o:}$ pH mean values are equal. $H_{a:}$ pH mean values are not equal. Soaking time of 24 hours is sufficient for the pH to stabilize.

The formulation or chemical analysis of the aggregate was diluted by the fact it varied over seventeen sources and was not consistent in any of those sources. But through the analysis, several formulas stood out as potentially reactive aggregates. The mean pH was significant in pits with and without lime. Lime was present in every reading above 9 pH. Aggregate chemistry in each pit may account for the variation in pH of the HMA mix above 9 pH. A good amount of disparity was found between the mixes with lime and those without lime. Numerous outliers were observed when lime was added and created

the right- tailed histogram and bell curve. These outliers were almost exclusively associated with pits 13 and 16 pointing to the chemistry of the aggregates. Pit 15 has these same characteristics, but to a lesser degree.

The continuous and categorical variables from Table 5 that were found to have a significant P-value with lime were pit, binder, lime, region, phagg-boiled and formula. And without lime were pit, oil, binder, region, phagg-boiled, and formula.

The final multivariate linear regression model was developed by first including all variables found to be significantly related to pH at an alpha of 0.15 in the bivariate screenings and then reducing the model to one in which only variables significant at an alpha of 0.05 remained. This was done for the models with lime and without lime. With all other variables held constant, the level of SiO_2 was found to be significantly correlated to pH of the HMA mix, $F(9,218) = 41.176$, $p = 0.000$. The size of the effect was such that on average, every one-unit increase in SiO_2 was associated with an increase of pH of 0.916 units, with hydrated lime being the primary contributor at 8.892 units. Since pH is a logarithmic scale, more research needs to be done as to the extent and significance of the numbers read, since going from an 8.5 pH to an 11 pH is 2.5 x 10 fold or a 25-fold increase in the concentration of hydrogen (H+) ions. From the literature review, as the H+ ions increase, the pH tends to vary toward an acidic concentration of ions, and calcium dissolution can take place in a pH range of 1-6. It is deduced that this pH change may be localized and site-specific with the reactive aggregate. From equation 1 of the literature review, the silicate lattice reaction with water imports excess hydroxyl ions, which is a typical hydrolytic reaction of the salt of a weak acid. This would explain that from the chemical formulas, silica dioxide at (20% - 48%) with various percentages of

calcium carbonate, calcium oxide, magnesium oxide, and aluminum trioxide, at (42-80%), may be producing acidic reactions and changing the pH levels.

Both residual plots and fit statistics indicate that the final models were poor fitting but have approximately 47-50% explanation value (with lime) and no value (without lime), because the algorithm broke down in explaining the chemical reaction at the asphalt binder/aggregate interface.

Conclusions

The first objective was to investigate the relationships of the components used in the HMA mixes in order to determine their individual contribution to the final pH within the HMA mixes. The chemistry of the aggregate can, when combined with lime, create a pH environment at the asphalt binder /aggregate interface conducive to the bond being compromised. The overall biggest factor affecting final pH is the addition of hydrated lime to the HMA mix, which is to be expected. Those mixes to which hydrated lime had been added exhibited a higher mean value of pH, but also tested with a much greater variability. Aggregate components such as SiO_2, $CaCO_3$ and CaO had an effect on final pH and added or subtracted from the final analysis. Knowledge of the aggregate chemistry and its potential to react with lime would improve the overall success of the bond and produce a longer lasting pavement. ASR/ACR should be investigated in suspect pits.

The second objective was to determine if the final pH of an HMA mix is a significant predictor of chemical reaction, which may lead to stripping damage in the asphalt binder/aggregate mix. The issue of moisture-induced or stripping damage has not been evaluated in this work.

Hydrated lime has a direct effect on the final pH of an HMA mixture of materials and, when combined with certain percentages and types of silicas and carbonates, can combine to increase or decrease the pH level. The use of hydrated lime in most mixes (85-90%) helps the bonding and improves the adhesion. In 10-15% of the mixes, the chemistry of the aggregate factors into the equation and, combined with the lime, creates chemical reactions in the mix, as indicated by exchange of H+ ions and OH-, causing an unstable interface between the asphalt binder and the aggregate. The higher pH values do predict detrimental chemical reactivity in the asphalt binder/aggregate mix.

The first research question was, does the pH of individual components of aggregates, asphalt binder, and additives point to and isolate suspect materials which chemically react and affect the final pH value?

Components such as hydrated lime, which is an additive and the chemistry of the aggregate (SiO_2, $CaCO_3$ and CaO), had the most significant effect on final pH value. The chemical composition of the aggregate in the source pit will have a positive or negative effect on the pH value, depending on the percentages of each mineral.

The second research question was, are final pH levels of mixed HMA materials (asphalt binders, additives, and aggregates) significant in predicting chemical reaction, which is suspected to affect the durability of the asphalt binder/aggregate mix?

The higher final pH values are predictors of chemical reaction, and those that seemed like outliers are the significant pH values that indicate other components are contributing to the chemical reaction, resulting in varied (lower or higher) final pH values.

The hypotheses that follow from the first and second question are

- H_o: There is no significant relationship between final pH values and chemical reaction of mixed HMA materials.
- H_a: There is a statistically significant relationship between final pH values and the chemical reaction of mixed HMA materials.

The null hypothesis would be rejected as the final pH is dependent upon the chemical reactions that take place at the asphalt binder and aggregate interface. The percentages of silica, carbonate, magnesium, aluminum etc. in the aggregate, along with the hydrated lime, affect the final pH value of the HMA mix.

The hypotheses that follow from the second question are

- H_o: There is no statistical linear model that predicts final pH values as a function of chemical reaction with water and the choice of components of the HMA mix.
- H_a: There is a statistical linear model that predicts final pH values as a function of chemical reactions with water and the choice of components of the HMA mix.

The null hypothesis would be rejected as there is, through a manual optimization procedure, a statistically significant mathematical equation developed for relating pH to two independent variables and one independent variable, respectfully. The final pH value is dependent upon the chemistry of the aggregate, with the addition of lime appearing to have the largest effect.

Recommendations

It is recommended that potential aggregate sources to be used in HMA mixtures are checked for the pH of the aggregate when boiled, and then checked as a loose HMA mixture of the aggregate and asphalt binder (with and without lime) for pH after 24-hours to determine the pH of the mixture and its magnitude. If the pH is high, i.e., above 9.0., it

is recommended that a chemical analysis be done on the aggregate to determine the percent of various minerals. The analysis of the aggregate could isolate moisture-susceptible and moisture-reactive aggregates (ASR/ACR). This upfront testing in the pit acceptance process could result in rejection of a questionable pit or source. Thus eliminating or modifying future failures in the product in service on the road.
More research needs to be done on additives other than hydrated lime that would decrease the chemical reaction and keep the pH low and help increase adhesion. Researched authors have concluded that a thin molecular layer of water remains on the aggregate (Appendix A).

From Table 18, it is stated that it would take temperatures higher than 500 degrees centigrade to burn off the last molecular layer of moisture **(**Little 2005). Since the highest temperature used in a hot mix plant producing asphalt is 135-145 degrees centigrade, it is evident that moisture remains on the aggregate. Additional research needs to be done on the effect of temperature on the components of the mix. Since reactions can take place when moisture is present, research is needed to assess the temperature range needed to eliminate the last molecular layer of moisture to allow the asphalt to bond more firmly with the rock surface without water present.

It is recommended that a series of tests be performed that start at 150 degrees centigrade and move upward at 25-50 degree centigrade increments on aggregates to determine the temperature at which all moisture is removed and to assess any damage to the aggregate. The results of this research would allow insight into the hot plant process which could aid in modifications to the equipment and process to remove the last molecular water layer. Tests would have to be performed to determine the contact time to

remove the water layer and length of additional drum to cool the aggregate so the asphalt could be introduced in the mix. This would eliminate one simply neglected or ignored source of moisture that may cause the pH instability to precipitate at the interface.

It is recommended that more research continue on the interface of the asphalt binder and the aggregate with lime and without lime, considering the chemistry of the aggregate and varying it with more silica and less calcium to more calcium and less silica on a reactive level to determine if pH changes from alkaline to acidic.

It is recommended that further investigation, using a control pit or two that are producing stable HMA mixes, be compared to the suspect pits, such as 13, 15, and 16 from this study, with high pH values and known HMA mix failures. Further investigation needs to be done to determine the reason for the high pH values found in the mixes in which lime had been added to HMA mixes from source pits 13, 15, and 16. The chemistry of the rock found in those sources and the effects when combined with hydrated lime in different percentages. This research could determine the underlying reason for these anomalies in the statistical analysis and conclusions presented in this paper.

APPENDIX A

RESEARCH RESULTS

Table 16 Initial pH Study Results on All Materials and Loose HMA Mixes

	pH Water	pH rock/w	rock boiled	Asp halt	Mix 1-64	Mix 2-l64	Mix 1l-64	Mix 2l-64
1. Hyrum	7.65	7.66	8.93	7.97	8.11	8.43	8.21	8.68
2. Trenton-Smithfield	7.97	7.88	8.89	8.10	8.29	8.43	8.21	8.42
3. Pt. East Ogden	7.99	8.13	8.89	8.23	8.50	8.43	8.58	8.81
4. Wells	7.76	7.93	8.63	8.04	8.12	8.47	8.12	8.65
5. Brigham City	7.93	7.84	8.71	7.96	8.38	8.26	8.50	9.24
6. McGuire-Ogden	7.99	7.85	8.80	8.33	8.26	8.16	8.83	9.42
7. Pt. of Mtn. S	8.17	7.86	8.78	8.06	8.29	8.29	8.25	8.80
8. BMG	8.07	7.94	8.53	8.10	8.11	8.25	8.28	8.56
9. Pt. of Mtn. G	7.83	8.06	8.72	8.22	8.41	8.33	8.51	8.71
10. Keigley	8.01	7.95	9.00	8.28	8.11	8.31	8.45	8.81
11. Roosevelt	7.58	7.92	8.85	8.15	8.16	8.23	8.24	8.53
12. Point East	8.11	8.06	8.70	7.85	7.97	8.19	8.60	9.73
13. Ferron	8.03	7.63	8.45	7.85	8.05	8.09	11.30	11.25
14. Centerfield	7.77	8.01	9.03	8.35	8.41	8.47	8.70	8.89
15. Cedar City	7.40	7.94	8.75	8.09	8.61	8.07	8.18	8.78
16. Moab	7.88	8.05	8.88	8.23	8.05	8.07	8.94	11.10
17. Elsinore	7.63	7.88	8.74	8.25	8.42	8.50	8.44	8.72
Distilled Water	6.15	8.21						
Bottled Water	6.63	8.61						
City Water	7.70	7.96						
Rain Water	6.74							
Asphalt in Distilled H20						l= Hydrated Lime		
1. 64-34	8.21					a= Polyphosphoric Acid		
2. 64-34	7.66							
1. 70-28 PPA	8.14							
2. 70-28 PPA	7.70							
1. 70-28	8.07							
2. 70-28	7.67							

Table 16 (Continued)

	Mix 1a-70	Mix 2a-70	Mix 1la-70	Mix 2la-70	Mix 1l-70	Mix 2l-70	Mix 1-70	Mix 2-70	48 hr. Mix 1l-70	48 hr. Mix 1-70
1.	8.48	8.33	8.53	8.55	8.70	8.50	8.45	8.24	8.75	8.60
2.	8.44	8.40	8.58	8.58	8.59	8.51	8.44	8.27	8.54	8.54
3.	8.39	8.38	8.70	8.67	8.74	8.65	8.43	8.25	8.74	8.61
4.	8.46	8.47	8.55	8.62	8.64	8.66	8.46	8.21	8.60	8.59
5.	8.35	8.37	8.88	9.01	8.84	8.63	8.46	8.18	8.97	8.47
6.	8.15	8.28	9.52	9.40	9.34	8.32	8.45	8.14	9.46	8.50
7.	8.28	8.35	8.58	8.73	9.48	8.65	8.39	8.34	9.27	8.45
8.	8.28	8.34	8.51	8.50	9.03	8.74	8.35	8.23	8.81	8.43
9.	8.23	8.42	8.65	9.14	8.70	9.94	8.45	8.30	8.60	8.53
10.	8.25	8.37	8.62	8.66	8.62	8.80	8.49	8.34	8.63	8.47
11.	8.25	8.31	8.42	8.52	8.56	8.78	8.35	8.14	8.51	8.39
12.	8.08	8.23	8.59	10.40	9.60	9.30	8.38	8.49	9.52	8.37
13.	8.07	8.24	10.63	10.86	10.71	10.31	8.22	8.25	10.57	8.20
14.	8.45	8.48	8.66	8.89	8.81	8.71	8.56	8.31	8.82	8.59
15.	8.12	8.17	8.64	8.87	8.75	9.02	8.33	8.08	8.63	8.40
16.	8.07	8.10	10.74	11.02	10.62	10.51	8.25	8.10	10.70	8.30
17.	8.47	8.42	8.66	8.75	8.75	8.70	8.51	8.04	8.81	8.59

l= Hydrated Lime a= Polyphosphoric Acid

Table 17 Chemical Analysis of Rock in Pits **(**Unpublished Data).

Pit or source	Chemical Analysis of Rock		
1	31% SiO_2	46% $CaCO_3$	36% CaO
2	72% SiO_2	20% $CaCO_3$	10% CaO
3	82% SiO_2	10% $CaCO_3$	6% CaO
4	82% SiO_2	10% $CaCO_3$	6% CaO
5	72% SiO_2	13% $CaCO_3$	7% Al_2O_3
6	82% SiO_2	6% $CaCO_3$	6% Al_2O_3
7	72% SiO_2	13% $CaCO_3$	7% Al_2O_3
8	72% SiO_2	13% $CaCO_3$	7% Al_2O_3
9	68% SiO_2	12% $CaCO_3$	13% MgO
10	40% SiO_2	44% $CaCO_3$	25% CaO
11	75% SiO_2	16% $CaCO_3$	10% CaO
12	68% SiO_2	12% $CaCO_3$	13% MgO
13	Limestone primarily No %		
14	59% SiO_2	15% CaO	15% MgO
15	31% SiO_2	56% $CaCO_3$	37% CaO
16	48% SiO_2	13% $CaCO_3$	12% Al_2O_3
17	49% SiO_2	10% $CaCO_3$	15% Al_2O_3

Table 18 A Summary of Theories and Mechanisms of Bitumen-Aggregate Adhesion (Little 2005)

(Weak) Boundary Layer Theory	• Low molecular weight organic contaminants on aggregate surface with low cohesive strength • Dust preventing effective wetting • Surface roughness and insufficient mixing temperature prevent effective wetting • Porosity acts as molecular sieve, absorbing low molecular fractions leaving polar species, forming a brittle interphase. • Dissolution of aggregate surface induced by pH of contacting water causes aggregate cohesive failure • Catalytic effect of aggregate on oxidative aging may cause brittle interphase • Long range polarization effect of aggregate on organic bitumen groups may cause more stable interphase
Mechanical Theory	• Macroscopic Scale • Contribution of size/ angularity/ gradation differs depending on magnitude of applied stress/ induced strain • Porosity: lock and key effect • Surface texture: redistribution of stresses and increased contact area • Microscopic scale • Fractal aggregate surface at microscopic scale • Phases of different hardness and morphology on bitumen surfaces
Electrostatic Theory	• Opposite charges attract • Surface charges develop in aqueous environments. At least a monolayer of water left on aggregate surfaces at temperatures below 500 to 1000°C • Electric double layers (EDLs) that interact or overlap, cause EDL forces that can attract or repel two surfaces. • Aggregate surfaces induce high pH environments in the presence of water. • pH of interface water affects surface charge of contacting surfaces. • Changes in surface charge affect the magnitude of electrostatic interactions.
Chemical Bonding Theory	• Lewis acids and bases interact through variety of bonds, which may include: covalent, donor-acceptor, coordination, and hydrogen bonding. • The nature of aggregate: More variable than bitumen and heterogeneous on macroscopic scale, comprising of different minerals with different functional groups. Aggregate dominates adhesion in bitumen-aggregate systems. • The nature of bitumen: Essentially a non-polar organic material with excess weak acidic compounds compared to basic compounds. • Interaction: The most prominent polar fraction in bitumen, acidic fraction, readily adsorbs onto aggregate surface forming bonds of variable durability, depending on the dominant mineral type in the aggregate under consideration. • Siliceous aggregates: Hydrogen bonds form with hydroxilated surfaces (silanol groups), which is easily displaced in the presence of water. • Calcareous aggregates: Free calcium prerequisite to form insoluble salt links, not easily displaced by water. • Intermediate aggregates: Siliceous and calcareous minerals or fractions, and/ or presence of other minerals. Transition metals form stronger hydrogen bonding, or if alkali earth metals present, ‘soaps’ or water-soluble salts form.

Table 18 (Continued)

Chemical Bonding Theory (continued)	• Additives • Lime added to bitumen: Tie up carboxylic acids (or acids) allowing nitrogen containing and other groups to form more durable bonds with siliceous surface groups. • Lime added to aggregate: Higher valence cations (Ca^{+2}) displaces lower valence cations on aggregate surface and bond with bitumen in a similar fashion as calcareous aggregate. • Amines added to bitumen: Nitrogen groups exhibit lone pairs of electrons that can take part in bonding. The strength of basic molecule depends on the hydrocarbon chain length; C_{18} for example, forms a strong basic molecule, easily protonized, forming a stable ionic/coordination bond. Naturally, the number of nitrogen head group's increases bond strength. • Coupling agents added to aggregate (organosilanes): Covalent bonds formed through hydrolyses, coupling, and condensation processes. • pH effect: influences donor-acceptor interactions which leads to unstable bonds within certain pH ranges.
Thermodynamic Theory	• Although it is listed as a theory, thermodynamics encompasses some of the theories/ mechanisms listed above and offers quantification following a macroscopic approach. • Free energy is minimized in order for system to approach an equilibrium state. • The nature of bitumen: Comprises of mobile hydrocarbons (polar and non-polar), which in contact with different polar surfaces may exhibit varying 'potential' surface free energies due to molecular orientation, depending on the chemistry of the contacting surface. • The nature of aggregate: Rigid atomic lattice structure comprises of different minerals each with its own intrinsic surface free energy. The energy of the total system is, however, additive. • Different extensions of classical thermodynamic theory exist. In the approach adopted in this research, microscopic contributions to adhesion are approximated on a macroscopic level by assigning surface energy components to each material. According to the van Oss-Chaudhury-Good theory, these are: a non-polar Lifshitz-van der Waals component, acid or electron acceptor component, and a base or electron donor component. • Physical surface chemistry combining rules or theories can be used estimate the free energy of adhesion between different materials. The theory by van Oss and co-workers are widely used and has been applied to bitumen-aggregate systems. The work of adhesion, or free energy of adhesion, can also be estimated in the presence of a third medium, such as water. • The energy approach is universal and allows incorporating these thermodynamic parameters into holistic, damage prediction models that include other important physical measurable properties such as compliance.

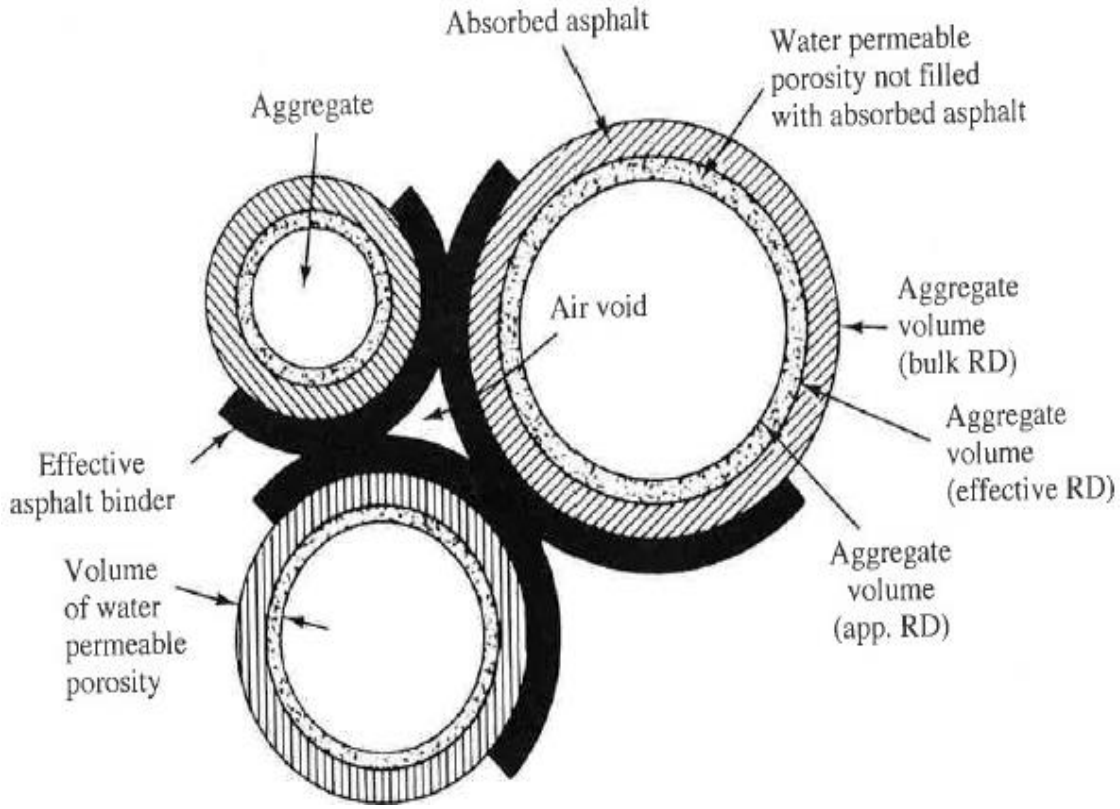

Figure 17 - Asphalt Mixture Diagram (Atkins 2003 4th Edition)

APPENDIX B

ON THE VARIABILITY OF RESULTS FROM THE

HAMBURG WHEEL TRACKER DEVICE

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On the Variability of Results from the Hamburg Wheel Tracker Device

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The Hamburg Wheel Tracker Device has been used for over thirty years to evaluate the performance of asphalt pavements in terms of rutting susceptibility and moisture damage (*Public Roads, 1998*). This paper focuses on using Linear Kneading Compactors and Hamburg Wheel-Tracker devices to make and test specimens of asphalt binder and aggregates from one source to determine any bias and typical errors related to the materials testing procedures used by various state testing laboratories. The objective is to determine whether the existing procedures can produce consistent and repeatable results, which can then be used in design and eventually in field acceptance tests. This report will provide a recommended procedure and precision statement for verifying the test specimen preparation and testing. In order to have consistent designs it is necessary to insure laboratories are performing at the same level.

Key Words: Uniformity, Repeatability, Procedure, Statistically Compatible, Bias

Introduction

The Hamburg Wheel Tracker Device (HWTD) has been used for over thirty years to evaluate the performance of pavements (*1*). However, most highway agencies have shied away from using the HWTD as a formal requirement for acceptance due to its lack of repeatability in its results and inability to predict pavement performance. One of the reasons creating these problems is the lack of standardization in the procedures used to prepare the samples. In other words there is a standard procedure for testing, but no procedure exists for preparing the specimen that will be used in the evaluation process. AASHTO T324: Standard Method of Test for Hamburg Wheel-Track Testing of Compacted Hot-Mix Asphalt (HMA) addresses the testing procedures, but it does not address the preparation of the specimen.

This paper will focus on the initial preparation process to determine if any part of the preparation is the cause of the large variability often seen in the results of the HWTD (*Izzo, 1997; Romero, 2010; Aschenbrener, 1993*). The goal of this paper will be to establish a standard practice for specimen preparation so that the results are within a reasonable standard deviation and to establish a precision and bias for the procedure. These results will allow highway agencies to use this practice to ensure rut resistant pavements that are not susceptible to moisture damage.

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Background

The use of the HWTD test requires test specimens be prepared using the same material and specifications. Thus the materials (aggregates and asphalt) are combined and compacted into a test specimen. The compacted specimen is then placed in the mold and secured in place inside the testing HWTD device The HWDT device is filled with water and the specimens submerged. Once the water has reached the correct temperature, the weighted wheels are lowered onto the specimens. The specimens are subjected to 20,000 passes of the weighted wheels in a water bath at a uniform temperature and the depth of indentation into the specimen is measured in millimeters (*Romero, 2008; Izzo, 1997*).A schematic is shown in *Figure 1*. Because the test was giving different results on samples prepared by the Department of Transportation (DOT) and those prepared by the local contractor's laboratories, concern was raised as to why the tests could not be performed with consistency. The department decided to run an inter-laboratory study (ILS) in an attempt to isolate the cause of the inconsistent results. After review of the preliminary test results, it was decided that variation in sample preparation was the probable cause of the inconsistencies and thus the hypothesis for the ILS.

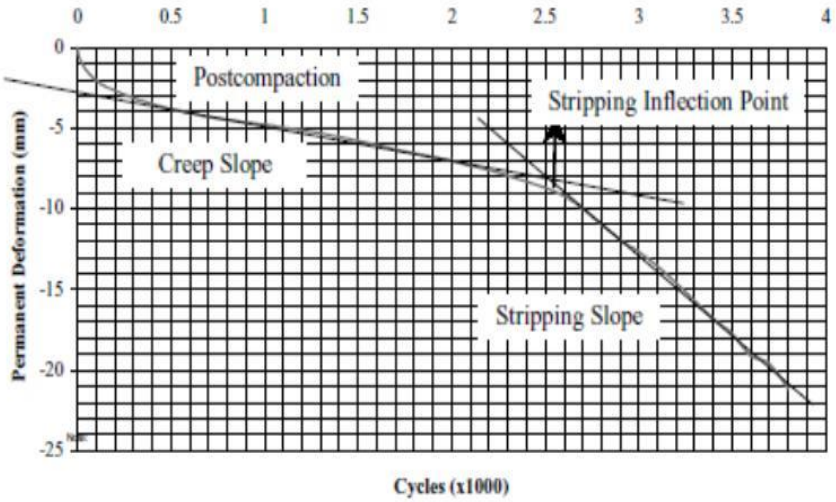

Figure 1: Schematic of HWDT results. (Solaimanian M. H. J., 2003)

The DOT uses the HWTD as a test method to determine the rutting and moisture susceptibility of (HMA) and specifies the following testing procedures. See *Figures 2 and 3*.

1. DOT Materials Manual- Part 8, Section 990 the Method of Test for Hamburg Wheel-Track testing of Compacted Hot Mix Asphalt (HMA). This procedure identifies DOT's modifications to AASHTO T 324, Hamburg Wheel-Track Testing of Hot Mix Asphalt (HMA),

2. AASHTO R 30, Standard practice for Mixture Conditioning of Hot-Mix Asphalt (HMA),

3. AASHTO T 209, Theoretical Maximum Specific Gravity and Density of Bituminous Paving Mixture Specimens, DOT Materials Manual –Part 8, Section 988- Guidelines for Laboratory Mixing of HMA.

Even though the DOT laboratories have been following these test procedures, the tests results have not been repeatable causing disputes between contractors and DOT's results

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Figure 2: Linear Kneading Compactor.

Figure 3: Hamburg Wheel Tracker Device.

Procedures

As previously mentioned, it was the hypothesis that most of the variability in the results was the inconsistent preparation of the specimens used for the test. The DOT opted to run an ILS series of tests with the intent to isolate the areas where the inconsistency of its sample preparation would result in error. The ILS testing involved a total of nine laboratories: a Central Materials Lab and the Eight DOT's Materials Laboratories participated in the testing. Each laboratory was provided enough of the same material (asphalt binder and aggregate) so that enough HWTD samples could be made to run the required tests. The **suggested guidelines** for a test program to confirm precision and bias of HWTD test procedures were:

- Select a commonly used marginal aggregate and an asphalt binder readily available from a known source.
- Obtain materials for test validation and certification. Obtain and store enough materials in sufficient quantities for present and future tests to minimize the effect of changing materials.
- Ship aggregate component to each participant laboratory. The sample size should be twice the amount needed to run the test.
- Ship the asphalt binders in approved containers to the laboratories. The asphalt binder is to be the type used during the initial mixture design stage.
- Compact the specimens to an air void level of 7.0 percent +/- 1%. The air voids should be reported with the test results for each specimen.
- Have the laboratories prepare, compact and run the test and fill out a HWTD Data form.
- Report the mean test results and Standard Deviation.
- Modify guidelines as the testing progresses if necessary.

The HWTD test data form is shown as a reference. Each laboratory was asked to keep a complete record of their procedure, fill in the blanks and make comments on the areas they felt were causing the results to vary. The results were then compiled, concerns and comments addressed and a new protocol for each succeeding test round was suggested. **The HWDT test data detail form used by each laboratory is included at the end of this paper for informational purposes only**.

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b. Record the time the slabs are submerged under water prior to the testing starting.

Summary of Hamburg results Test Cycle # 2

The Central Laboratory was to compact the slabs from windrow samples from the given aggregate source and then deliver them to the individual laboratories to run the test. The range of the test values in the first test cycle was 15.98 mm and the range in the second test cycle was 4.12 mm. This was a decrease in range value of 11.86 mm. **A decrease of almost 75%.This essentially verified that the variation was in the compaction procedures used by the participating laboratories.**

Background of Test Cycle # 3

It was observed from test cycle #2 the maintaining temperature in the linear kneading compactor, and the amount of material for the specimen mold, was critical to uniform compaction. When the mold plates were preheated and mold heaters were not present in the compactor, it was observed that it took longer to place the material and start the compaction and therefore more temperature was lost. Cooler temperatures caused more density variation resulting in greater test variability. The ability to provide the right amount of material also became crucial to the compaction effort and desired density.

Based on the experience from preparation of the specimens and dialogue of the preparers, it was believed that these two factors along with the heating of the molds were causing most of the deviations in test results. The amount of material was initially being obtained by trial and error, with poor results. The method was then changed to a calculation of the mold volume (V) with the compaction roller running hard against the top of the mold, determining the maximum theoretical specific gravity (Gs), determining a density factor (.93) and obtaining the weight of the specimen(W) using the formula V*Gs*0.93=W. The weighed material is placed in the mold and the specimen compacted until the roller is on the rim of the mold. The density of the specimen is then verified. With these adjustments in the initial heating and compaction procedure the individual laboratories prepared the specimens to run test cycle #3.

Summary of Hamburg results Test Cycle # 3

The individual laboratories were to compact the specimens from Central Laboratory prepared samples from the given aggregate source.

Validation Tests of Procedures used for compaction

Background of Validation Test Cycles # 4 and # 5

The next two validation test cycles are data gathering, to find out if the changes have allowed for more uniform results and that the testing could be replicated. Test Cycle # 4 and # 5 were performed with the same criteria as Test Cycle # 3.

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Data Results for all the ILS tests are shown in Table A.

***Results and Findings*:**

Five ILS test cycles were necessary to obtain enough information to lower the variability. Three initial testing cycles and two additional validation cycles were run to insure repeatability.

Background of ILS Test Cycle #1

The first test cycle was initiated in June 2005 using the modification to AASHTO by a DOT's Materials Manual Part 8-990 to reflect procedure each laboratory had been using previously. The individual laboratories were to prepare the samples themselves and run the tests, as they understood the procedures. The results used for analysis were the maximum impression in millimeters, since that is the criteria the DOT had chosen for acceptance of the mixture.

Summary of Hamburg results Test Cycle #1

The individual laboratories were to compact the test specimen slabs from windrow gathered samples from the given aggregate source. The aggregate from this source is marginal when tested against aggregate specifications. The asphalt binder was obtain from the supplier to the given aggregate hot plant and certified by the Central laboratory for the testing.

The concerns reported by the participant laboratories on the sample as they prepared and ran the specimens were:

- What size of specimen is needed for 93% compaction?
- Do the plates need to be heated to compaction temperature prior to compaction of the specimen?
- Is it necessary to obtain a uniformly compacted specimen?
- Is sealing the edges properly around the mold necessary?
- When to place specimens in the wheel-tracker device to equalize temperature.
- When time limits are placed on the test, from start of heating of sample for compaction to start of wheel-tracker cycles, it makes the testing cycle at night or odd hours.
- Is the 7% voids only for laboratory compacted specimens?
- Time from oven to compaction start may result in a drop in temperature.

As a result of these concerns and observations, the procedures were modified for the next test cycle.

Background of Test Cycle #2

After the input from the first test cycle, the second test cycle specimens were prepared using the original materials. However, this time all of the specimens were all compacted at DOT Central Laboratory and then delivered to the individual participants to run the Hamburg Wheel-Tracker test. The instructions were as follows:

a. Prepare the specimens with Plaster of Paris in the testing trays the afternoon or prior to quitting time before testing the next morning.

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Table A Results of Test and Validation Test Cycles

TC-1	Central	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Range	C of Var.
Lt. Max	4.06	19.90	15.30	4.50	9.04	16.35	X	X	X		
Rt. Max	4.61	20.04	8.42	9.50	6.11	13.14	X	X	X		
										15.98	0.54
TC-2											
Lt. Max (1)	5.13	3.33	4.97	5.03	5.67	4.65	X	X	X		
Rt. Max (1)	4.23	5.97	4.33	4.56	4.25	4.49	X	X	X		
Lt. Max (2)	7.45										
Rt. Max (2)	4.09										
Lt. Max (3)	3.47										
Rt. Max (3)	4.57										
Lt. Max (4)	3.64										
Rt. Max (4)	3.87										
Lt. Max (5)	3.95										
Rt. Max (5)	4.34										
										4.12	0.21
TC-3											
Lt. Max	2.60	X	3.24	3.35	4.28	X	7.74	7.49	3.08		
Rt. Max	2.58	X	3.23	3.72	4.61	X	9.21	9.46	4.27		
										6.88	0.50
VTTC-4											
Lt. Max (1)	6.67	6.34	4.64	8.87	10.91	6.09	11.65	8.65	X		
Rt. Max (1)	5.04	13.57	3.90	6.75	9.95	9.40	4.59	7.89	X		
Lt. Max (2)	6.58										
Rt. Max (2)	6.74										
Lt. Max (3)	7.14										

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ANOVA

Source of Variation	SS	df	MS	F	P-value	F-Crit.
Between Groups	0.25088	1	0.25088	0.275367	0.606157	4.413863
Within Groups	16.39934	18	0.911074			
Total	**16.65022**	**19**				

Result: Since F crit >> F and P >> than 0.05, the Null Hypothesis cannot be rejected.

Conclusion:

There is no difference between Central Laboratory running the HWTD on the Central Laboratory prepared specimen and the other eight laboratories running a Central Laboratory prepared specimen. This implies that the differences are not in the Hamburg Wheel Tracker Device. Any of the results of specimens run at Central Laboratory, using the new protocol, can be combined with the results of any specimens run in other labs, on Central Laboratory prepared specimens, to obtain the precision of test for a single lab about the average rut depth.

Additional results run under the new protocol after Test Cycle Two by the Central Laboratory. The results of TC#3 and VTTC #4 & VTTC#5 ran by Central.

Central: 2.60, 2.58, 6.67, 5.04, 6.58, 6.74, 7.14, 5.30, 6.22, 5.69, 8.00 and 4.66.

Mean: 5.60

Range: 5.42

Standard Deviation: 1.34

Variance: 0.24

Conclusion: For a test mean of 5.6, a single laboratory precision SD should be +/- 1.34. If the variance (1S %) = SD/Mean + 0.24 (24%) and if the mean = 10, the SD_{10} = 2.4. These results are certainly consistent with TC#3.VT# 4 and VT# 5 results present an even tighter grouping.

Thus the precision statement for a single lab (1S %) = 24 % and for multiple labs (2S %) = (1S %)*2.8 = 67%.

Summary of Observations

The specimens, from those individual testing laboratories that did not following the instructions in the Manual of Instruction, resulted in tests which gave erroneous or outlier answers. The tests from one lab were only run for

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Rt. Max (3)	5.30										
										7.75	0.30
VTTC-5											
Lt. Max (1)	6.22	9.10	5.68	3.70	7.70	6.42	20.76	0.00	3.48		
Rt. Max (1)	5.69	5.32	7.92	4.28	5.82	8.47	9.46	4.93	3.00		
Lt. Max (2)	8.00										
Rt. Max (2)	4.66										
										5.76	0.27

X = Invalid test data or data not submitted. Units are in millimeters. Shaded numbers were outliers and not used.

SUMMARY of Test Cycle Tests 1-3 and Validation Tests Cycles 4&5:

TC # 1	TC # 2	TC # 3	VTTC # 4	VTTC # 5
Mean= 10.91mm	**M = 4.60mm**	**M = 4.92mm**	**M = 7.22mm**	**M = 6.46mm**
Std. Dev.= 5.88	**SD = 0.95**	**SD = 2.45**	**SD = 2.20**	**SD = 1.77**
Range = 15.98	**Range = 4.12**	**Range = 6.88**	**Range = 7.75**	**Range = 5.76**
C of V = 0.54	**C of V = 0.21**	**C of V = 0.50**	**C of V = 0.30**	**C of V = 0.27**

ANALYSIS OF VARIABILITY IN HWTD RESULTS

From the results of Test Cycle # 2 an analysis was performed to determine if there were any differences between results of the Central Laboratory and the results of the other eight participating laboratories. Analysis shows that there were no statistical differences between the Central laboratory tests results and the other laboratory test results.

Analysis of TC # 2 Central laboratory results and other eight laboratory results:

Central laboratory results: 5.13, 4.23, 7.45, 4.09, 3.74, 4.57, 3.64, 3.87, 3.95 and 4.34.

Other Laboratory results: 3.33, 5.97, 4.97, 4.33, 5.03, 4.56, 5.67, 4.25, 4.65 and 4.49

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance	Range
Central	10	45.01	4.501	1.265277	3.81
Other Labs	10	47.25	4.725	0.556872	2.64

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10,000 passes instead of the 20,000 passes that the other labs were completing and therefore the tests were invalid. The location of equipment in relation to the oven is an important factor in preventing cooling of the specimens before compaction. The ability to load the Linear Kneading Compactor specimen molds from both sides of the compactor eliminates a time factor between the concurrently processed specimens. Heating of the compaction plates and limiting the time from the oven to start of compaction reduces the loss of heat and the possibility of a heat sink by the Linear Kneading Compactor. The care of calculating and measuring the amount of material for loading the compaction molds is essential to obtaining a uniform density across the specimen. The procedure for preparing and placing the specimens in the Hamburg Wheel Tracker Device is also important to the consistent results that were being sought in the ruggedness tests. The time the specimen is in the water and the temperature of the water were factors in the process that could not be over looked to standardize the procedure. Temperatures of the prepared specimens were taken before placing them in the water and time logged until they were at the testing temperature. The time for the specimens to come to uniform temperature was determined to be one-half an hour when the water in the Hamburg Wheel Tracker Device was at testing temperature. It is important to have a way to heat the water (a hot water heater) to keep the time of the test to a reasonable period of time for the specimen. The statistical data shows that the equipment is capable of performing the compaction, rutting and moisture damage test as designed and that the errors that were being introduced were from the preparation and handling of the specimens. This was evident from the 75% drop in range values from TC#1 testing to TC#2 testing results. When specific limits were adhered to the results became more uniform (Romero, 2008).

Conclusions

The compaction process can introduce variability by non-uniform density across the specimen. Calculation and measuring or weighing of material for the mold is extremely important. Compaction to top rim of mold is necessary for uniform compaction. Heating of the compaction plates and the time from oven to loading and compaction of molds is critical. With proper compaction procedures, the HWTD will provide consistent results. Rutting and moisture susceptibility results will be reliable.

Precision and bias for this procedure can be stated at (1S%= 24% and 2S%= 67%).

Recommendations

The placement and installation of Linear Kneading Compactor should be done to insure the shortest distance from the oven to the compactor is maintained, to allow a maximum temperature in the mix. Training for technicians is necessary, to insure each technician maintains consistency in procedure. Adequate compaction temperature should be maintained by being efficient in movements and preparation. Uniformly load the compaction mold with the proper amount of calculated material to insure proper densification of the specimen. Follow the Manual of Instruction to insure consistency. It is imperative to take compaction variability out of the test so the materials can be evaluated correctly, as the HWTD is very consistent in the procedure. Density should be within +/- 1/4% across the specimen to achieve accurate results. Density between labs should be with +/- 1/2%.

FOR INFORMATION ONLY

Hamburg Wheel Tracker Device Test Data report form

Lab: Date Test begins: Technician:

Sample heated for combination and splitting

Begin:

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Remove from oven: Time Temp

Comments

Did you hold the sample at low temp? Explain.

Slab Preparation Date:

Reheat

Slab # 1 Begin:
Remove from oven Time Temp

Slab # 2 Begin: Time Temp

Remove from oven Time
Temperature

How did you heat the plates? How did you heat the molds?

Comments:

Compaction

Slab # 1: Begin Time End Tim
Size H/W/T
Slab # 2: Begin Time End Tim
Size H/W/T
Temperature
How did you determine the temperature at the beginning of compaction?
How did you determine the temperature at the end of compaction?
Comments:
Cooling
Slab # 1: Begin Time End Tim
Slab # 2: Begin Time End Tim
Comments: (any special handling)
Set Slab in Mounting Tray
Slab # 1: Begin Time End Tim
Slab # 2: Begin Time End Tim
Comments: (centering techniques)
Hamburg Wheel Tracker Test Date:
Time tank is filled:
Time tank reaches temperature:
Time slabs are placed in device:
Micro Control LVDT readout:
Time of first tracking cycle:
Time of end tracking cycle:
Comments:
Other comments on the procedure:

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APPENDIX C

SIGNIFICANCE OF pH VARIANCE IN PREDICTING CHEMICAL REACTION IN HOT MIX ASPHALT

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Significance of pH Variance in Predicting Chemical Reaction in Hot Mix Asphalt

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Abstract: Hot mix asphalt (HMA) is a combination of siliceous, calcareous, or intermediate aggregate materials from selected sources, blended with formulated asphalt binders from various asphalt binder producers. These components are modified by additional additives to enhance the bonding of the binders and aggregates. Concern over moisture damage (stripping), defined as the loss of strength and durability in asphalt mixtures when the binder separates from the aggregate, has prompted years of research into a variety of failure mechanisms. Prominent in these failure mechanisms is the pH at the binder–aggregate interface. This technical paper addresses the pH variance of individual components and loose blended HMA mixes from 17 selected material sources and 2 asphalt binder sources to assess the pH of any chemical reactivity. The main objective of the paper is to determine whether pH variances of individual components or mixed HMA materials (asphalt binder, aggregate, and additives) point to suspect components or combinations that cause a chemical reaction and, thus, instability or moisture-induced stripping at the aggregate interface. This research may point to alkali-silica and alkali-carbonate reactivity of aggregates as potential contributing causes of moisture-induced damage in HMA mixes. Statistical analysis is used to interpret the interaction of the independent variables and indicate contributing components correlating with the pH variance and chemical reaction. **DOI: 10.1061/(ASCE)MT.1943-5533.0001391.** *© 2015 American Society of Civil Engineers.*

Author keywords: pH; Hot mix asphalt; Silica; Hydrated lime; Variables; Aggregates.

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Introduction

The current design procedure for hot mix asphalt (HMA) requires the contractor to submit for verification a mix design to a DOT testing laboratory. Mix designs that fail verification must be redesigned, resubmitted, and reverified. This verification process is costly and time consuming. In addition, verified mix designs that use marginal materials in their production process will, over time, when placed as pavement, prematurely fail in the field, causing pavement damage and costly repairs. This research investigates pH variance as an early evaluation tool that would identify suspect components of HMA design mixes that contribute to chemical reaction and, thus, loss of adhesion or stripping of the asphalt binder from the aggregate in the mix. This research is supported by current theory, which describes the adhesion of bitumen and aggregate in the presence of water, causing a chemical reaction at the interface. Materials found in the state of Utah, including both aggregates and asphalt binders, owing to their availability for testing, are the source materials used in this research. These Utah materials are similar in characteristics and chemical nature to the aggregate and asphalt sources used in all countries, which makes the research relevant for the industry worldwide. ASTM and AASHTO preparation and test methods will be used to prepare samples. Measured pH laboratory test values of individual components and of HMA loose mix samples are the basis for carrying out this research.

A multivariate linear regression statistical model and analysis using IBM *SPSS v 21.0* is used to quantify the test results.

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Categorical Variables

1. Aggregate pit or source: the 17 selected aggregate sources at various locations.
2. Oil (type): defined by a 70-28 or 64-34 Strategic Highway Research Program grade.
3. Asphalt binder (source): producer who supplied the oil.
4. Hydrated lime: an additive added to the HMA mix to help increase the adhesion between the asphalt binder and the aggregate.
5. PPA (polyphosphoric acid): additive added to the formulation of the oil.
6. Time: hours the specimen was soaked in distilled water.
7. Region: either north or south classification of aggregate pits.
8. Formula: percentages of minerals over 5% from each aggregate pit.
9. The continuous variables in this study were pH (dependent variable), pHagg-boiled, SiO_2, $CaCO_3$, CaO, Al_2O_3, and MgO.
10. pHagg-boiled: aggregates boiled in water and soaked for 24 h.
11. SiO_2, $CaCO_3$, CaO, Al_2O_3, MgO: chemical composition of aggregate minerals in each pit.

Objectives

1. Evaluate the relationships of the components used in the HMA mixes in order to determine their individual contribution to the final pH within the HMA mixes; and
2. Determine whether the final pH of a HMA mix is a significant predictor of a chemical reaction that may lead to stripping damage and less durability in the asphalt binder/aggregate mix.

Research Questions

If it is suspected that pH levels affect the durability of asphalt mixtures:

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1. Does the pH of individual components of aggregates, asphalt binder, and additives point to and isolate the suspect materials that react chemically and affect the final pH value?
2. Are the final pH levels of mixed HMA materials (asphalt binders, additives, and aggregates) significant predictors of a chemical reaction that is suspected to affect the durability of the asphalt binder/aggregate mix?

Hypothesis

The hypothesis that followed from these questions is as follows:

1. H_o: There is no statistical linear model that predicts final pH values as a function of chemical reaction and the choice of individual components of a HMA mix.
2. H_a: There is a statistical linear model that predicts final pH values as a function of chemical reaction and the choice of individual components of the HMA mix.

The main theory of this work is that variances in pH readings of mixed HMA materials (asphalt binder and aggregate) are an early predictor (with $P = 0.05$ probability confidence) of a chemical reaction at the asphalt binder/aggregate interface due to moisture. The mineralogy or petrography of a rock or aggregate, when moisture is present, can induce ASR/ACR reactions, which produces instability at the binder/aggregate interface. Water causes a reaction and formation of a gel, which results in a rise in pH at the interface between the asphalt binder and aggregate in the HMA mix, causing failure by chemical reaction that breaks the mechanical bond between the binder and the aggregate. The amount of silica content or the silica phase on the rock mineralogy, as well as the amount of carbonate, is revealed by the chemistry of the aggregates in the various pits.

With the final pavement layer being the most expensive layer in a highway project, investigation of moisture damage or stripping using the associated theories and mechanisms are of particular interest in exploring. This study of pH may provide an early, inexpensive, practical solution for choosing or eliminating certain HMA materials for use in design and verification processes, which may ultimately lead to the production of a longer lasting pavement structure.

Methodology

Testing was done using distilled water as the test medium. The pH value of the water used at the various HMA batch plants was taken to eliminate batch plant water as a contributing source of high/low pH values. Two different asphalt binders, from asphalt binder sources approved by the Utah DOT asphalt testing laboratory, were obtained for testing and preparing the mixed specimens. Hydrated lime, as an additive, was obtained to evaluate its contribution to the pH of the HMA mixes.

The pH measurements were recorded for the individual components: the two asphalt binder grades, the 17 different aggregate sources, unboiled and boiled. Loose mix HMA specimens, including HMA mixes with and without hydrated lime added and with and without polyphosphoric acid formulated in the asphalt binders, were prepared, and the pH of the combined loose HMA mixes of the asphalt binder and aggregates were recorded.

The mixed specimens represent typical asphalt–aggregate combinations used in highway construction.

To obtain the pH of individual components and combined HMA mixes, the following steps were followed:

1. Record the pH value of the 17 individual aggregate sources soaked in distilled water for 24 h.
2. Record the pH value of the individual water sources associated with existing HMA plants that use the aggregates from the 17 sources.
3. Record the pH value of the individual asphalt binders, with and without PPA.
4. Combine the individual components into loose HMA mix specimens for testing.
5. Record the final pH value of the HMA mix specimens with and without lime added to the mix. These specimens will be soaked for 24 h in distilled water.
6. Statistically analyze the pH values and identify high-pH contributing components.

The pH test values of these mixtures were analyzed using a statistical program to determine the strength of the relationship between pH values and the contribution of each of the individual components comprising the loose HMA mixes with and without lime added. The HMA mixes with lime were prepared at 1% lime added by weight. The aggregates from each pit were assessed by the percentage of mineral property shown by a chemical analysis of the pit aggregates (Table 1) (M. A. Rigby unpublished data, 2010). The aggregate samples were tested unmixed at 200–250 g by weight. HMA samples were mixed at 150–250 g by weight for testing and asphalt binder at 100 g by weight.

The preparation procedure followed AASHTO T-182-84 (AASHTO 2002), which is used to prepare loose asphalt mixes. A calibrated pH meter (accuracy ±0.01%) was used to measure the pH test values.

Individual components (aggregate at 250 g mass) (asphalt binders 70-28 and 64-34 at 100 g mass) were tested first and placed in containers, and distilled water was added to the same level in each container (300 mL). The specimens were soaked for 24 h and the pH reading taken and recorded. Then aggregates, asphalt binders 70-28 and 64-34, and hydrated lime/no hydrated lime were mixed together to produce the individual loose HMA specimens (HMA mix at 150–250 g mass). After cooling, they were placed in containers and distilled water added to the same level in each container (300 mL).

The mixing was completed using mixers, asphalt heating pots, drying ovens, and certified scales that are used to mix and verify contractor-submitted mix designs for use on highways.

The recorded pH value of each component submerged in distilled water established a pH baseline of the individual mix components (Fig. 1). These combined components were allowed to soak for 24 h in 300 mL distilled water, and the final pH of each

Table 1. Chemical Analysis of Rock in Pits Studied (M. A. Rigby, Unpublished Data, 2010); Only Percentages over 5%

Pit or source	Chemical analysis of rock		
1	31% SiO_2	46% $CaCO_3$	36% CaO
2	72% SiO_2	20% $CaCO_3$	10% CaO
3	82% SiO_2	10% $CaCO_3$	6% CaO
4	82% SiO_2	10% $CaCO_3$	6% CaO
5	72% SiO_2	13% $CaCO_3$	7% Al_2O_3
6	82% SiO_2	6% $CaCO_3$	6% Al_2O_3
7	72% SiO_2	13% $CaCO_3$	7% Al_2O_3
8	72% SiO_2	13% $CaCO_3$	7% Al_2O_3
9	68% SiO_2	12% $CaCO_3$	13% MgO
10	40% SiO_2	44% $CaCO_3$	25% CaO
11	75% SiO_2	16% $CaCO_3$	10% CaO
12	68% SiO_2	12% $CaCO_3$	13% MgO
13	Limestone primarily number (%)	—	—
14	59% SiO_2	15% CaO	15% MgO
15	31% SiO_2	56% $CaCO_3$	37% CaO
16	48% SiO_2	13% $CaCO_3$	12% Al_2O_3
17	49% SiO_2	10% $CaCO_3$	15% Al_2O_3

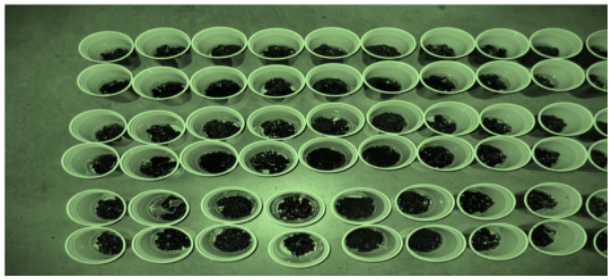

Fig. 1. Samples immersed in distilled water

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sample was recorded. An additional 24 h of soaking time was allowed for 34 specimens of mix 1-70-28 without lime and mix 1l-70-28 with lime specimens to see whether the pH value remained the same or increased in value to determine whether the testing period of 24 h was sufficient to allow infiltration of the water. A paired sample *t*-test was conducted to see whether the pH readings at 24 and 48 h were actually different. The *t*-value determined whether 24 h of soaking was a sufficient amount of time for the mix to stabilize for an accurate pH reading. H_o:pH mean values are equal; H_a:pH mean values are not equal.

Replicate pH readings of the same specimen were not taken because the pH meter was calibrated and verified before each set of readings. The pH meter is accurate to $\pm 0.01\%$, and therefore any experimental error was deemed to be negligible. All recorded readings are shown in Tables 2 and 3.

Chemical analysis data from a draft report to the Utah DOT on the mineralogical properties of course aggregate corresponded to the same sources used in this research. These data, which were used with the permission of Utah DOT, were incorporated to allow the interpretation of the pH results with the chemical analysis on the aggregate from the same source. The mineralogical properties of course aggregates from Source Pits 1, 2, 3, 4, 5, 6, 8, 9, 11, 12, 15, 16, and 17 were obtained from a draft report to the Utah DOT (M. A. Rigby, unpublished data, 2010). The results are presented in the appendix (Table 1).

Statistical Analysis of pH Data Using IBM SPSS Version 21

To investigate the effects of various components on the pH of the HMA mix, a regression analysis method was used with maximum-likelihood estimation rather than linear discriminant analysis since it is unlikely that the two methods would give markedly different results and the maximum-likelihood method is preferable where

Table 2. Initial pH Study Results of Aggregates, Water, Asphalt Binders, and Loose HMA 64-34 Mixes

Parameters	pH water	pH rock/w	Rock boiled	Asphalt	Mix 1-64	Mix 2-l64	Mix 1l-64	Mix 2l-64
1. Hyrum	7.65	7.66	8.93	7.97	8.11	8.43	8.21	8.68
2. Trenton-Smithfield	7.97	7.88	8.89	8.10	8.29	8.43	8.21	8.42
3. Pt. East Ogden	7.99	8.13	8.89	8.23	8.50	8.43	8.58	8.81
4. Wells	7.76	7.93	8.63	8.04	8.12	8.47	8.12	8.65
5. Brigham City	7.93	7.84	8.71	7.96	8.38	8.26	8.50	9.24
6. McGuire-Ogden	7.99	7.85	8.80	8.33	8.26	8.16	8.83	9.42
7. Pt. of Mtn. S	8.17	7.86	8.78	8.06	8.29	8.29	8.25	8.80
8. BMG	8.07	7.94	8.53	8.10	8.11	8.25	8.28	8.56
9. Pt. of Mtn. G	7.83	8.06	8.72	8.22	8.41	8.33	8.51	8.71
10. Keigley	8.01	7.95	9.00	8.28	8.11	8.31	8.45	8.81
11. Roosevelt	7.58	7.92	8.85	8.15	8.16	8.23	8.24	8.53
12. Point East	8.11	8.06	8.70	7.85	7.97	8.19	8.60	9.73
13. Ferron	8.03	7.63	8.45	7.85	8.05	8.09	11.30	11.25
14. Centerfield	7.77	8.01	9.03	8.35	8.41	8.47	8.70	8.89
15. Cedar City	7.40	7.94	8.75	8.09	8.61	8.07	8.18	8.78
16. Moab	7.88	8.05	8.88	8.23	8.05	8.07	8.94	11.10
17. Elsinore	7.63	7.88	8.74	8.25	8.42	8.50	8.44	8.72
Distilled water	6.15	8.21	—	—	—	—	—	—
Bottled water	6.63	8.61	—	—	—	—	—	—
City water	7.70	7.96	—	—	—	—	—	—
Rain water	6.74	—	—	—	—	—	—	—
			Asphalt in distilled H20					
1. 64-34	8.21	—	—	—	—	—	—	—
2. 64-34	7.66	—	—	—	—	—	—	—
1. 70-28 PPA	8.14	—	—	—	—	—	—	—
2. 70-28 PPA	7.70	—	—	—	—	—	—	—
1. 70-28	8.07	—	—	—	—	—	—	—
2. 70-28	7.67	—	—	—	—	—	—	—

Note: l = hydrated lime; *a* = polyphosphoric acid.

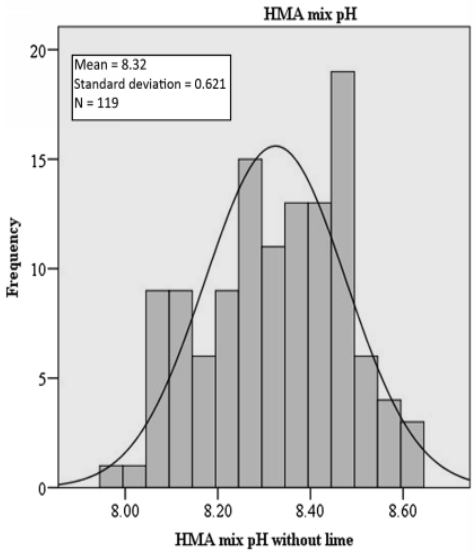

Fig. 3. Histogram and mean of HMA mix pH without lime

The histogram plot of the HMA mix pH with lime is skewed to the right, and the plot without lime is a more uniform normal distribution. The mean for the HMA mix pH with lime is 8.65, whereas the median is 8.495. This median is much closer to the mean and median of the HMA mix pH without lime at 8.32 and 8.34, respectively. Identifying the reason for the high pH is the focus of the remaining discussion and emphasis of this paper. The continuous variables in this study were the pH (the dependent variable), pHagg-boiled (related to the chemical characteristics of the aggregate), SiO_2, $CaCO_3$, CaO, Al_2O_3, and MgO or a formula expressed as percentages of the chemical analysis of the rock. The outputs of the summary statistics are shown in Tables 4 and 5.

Observations from the descriptive continuous variables with lime are as follows:

1. A skew that has an absolute value greater than one is regarded as significant. An incredibly high positive skew is the dependent-variable HMA mix pH (2.506). Because of the extreme skew, the median will be used more than the mean to describe the central tendency;
2. This is problematic because regression work turns out best when the dependent variable has a normal distribution.
3. The observations show that quite a few pH values were above the mean, suggesting more investigation is necessary for clarifying the reasons or cause of the skew.

Observations from the descriptive continuous variables without lime are as follows:

1. There was no right-tailed skew for pH less than 1, but right-tailed skews remained for the $CaCO_3$, CaO, and Al_20_3 continuous variables, which is regarded as significant.
2. A model for the dependent-variable HMA mix pH should be more reliable since the underlying assumption of normality appears to be met.
3. The addition of lime accounted for ALL of the specimens in which the pH exceeded 9 (Fig. 4). This appears to be a primary factor affecting the pH of the final mix.

The mean plots of HMA mix versus location pit or source are shown (Figs. 5 and 6), with and without lime.

A comparison of the locations, pits, or sources, with and without hydrated lime added, points to four locations, pits, or sources that have pH readings significantly different when the lime is present. Pits 13 and 16 have pH readings with lime averaging near 9.4 but drop to 8.15 without lime added. Pits 14 and 17 with lime have pH readings near 8.60 but drop to 8.45 without lime added, a 13 and 2% decrease, respectively, in pH. The chemistry of Pit 13 is predominantly limestone, and Pit 16 is 48% SiO_2, 13% $CaCO_3$, and 12% Al_2O_3. Pit 14 is 59% SiO_2, 15% CaO, and 15% MgO, and Pit 17 is 49% SiO_2, 10% $CaCO_3$, and 15% Al_2O_3. The remaining locations or pits vary approximately 2% with or without hydrated

Table 4. Output Summary Statistics: Continuous Variables with Lime

	N	Minimum	Maximum	Mean	Standard deviation	Skewness
Parameter	Statistic	Statistic	Statistic	Statistic	Statistic	Statistic
HMA mix pH	238	7.97	11.30	8.6508	0.62114	2.506
SiO_2	238	0.20	0.82	0.6018	0.19335	−0.692
$CaCO_3$	238	0.05	0.80	0.2093	0.21143	1.612
CaO	238	0.00	0.34	0.1044	0.08931	1.416
Al_2O_3	238	0.00	0.15	0.0608	0.03194	1.190
MgO	238	0.00	0.15	0.0487	0.05105	0.849
Valid *N* (list wise)	238	—	—	—	—	—

Table 5. Output Summary Statistics: Continuous Variables without Lime

	N	Minimum	Maximum	Mean	Standard deviation	Skewness
Parameter	Statistic	Statistic	Statistic	Statistic	Statistic	Statistic
HMA mix pH	119	7.97	8.61	8.3247	0.15215	−0.221
SiO_2	119	0.20	0.82	0.6018	0.19376	−0.696
$CaCO_3$	119	0.05	0.80	0.2093	0.21187	1.622
CaO	119	0.00	0.34	0.1044	0.08950	1.425
Al_2O_3	119	0.00	0.15	0.0608	0.03201	1.197
MgO	119	0.00	0.15	0.0487	0.05115	0.855
Valid *N* (list wise)	—	—	—	—	—	—

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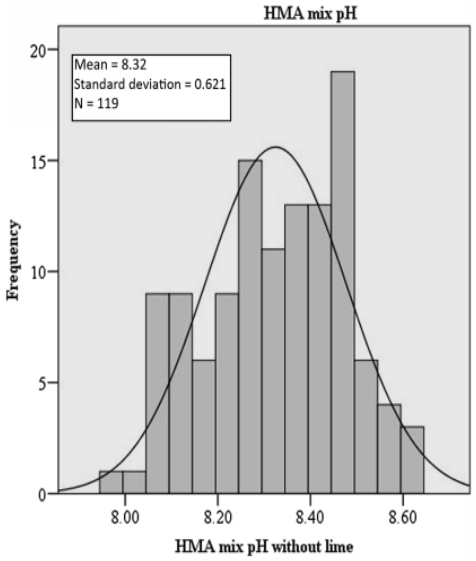

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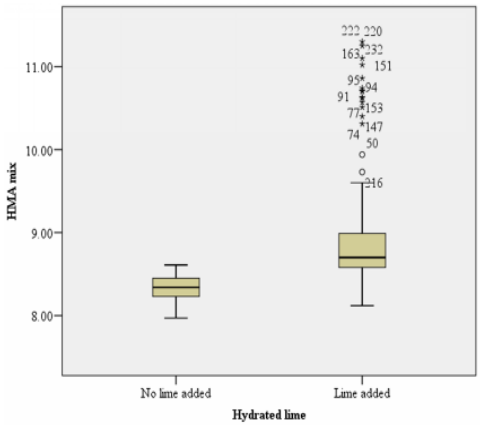

Fig. 4. Comparison plot of HMA mix pH with and without hydration

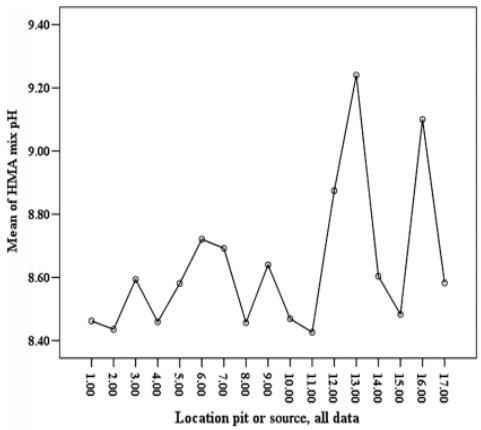

Fig. 5. Mean plot of HMA mixes—all data versus location pit or source

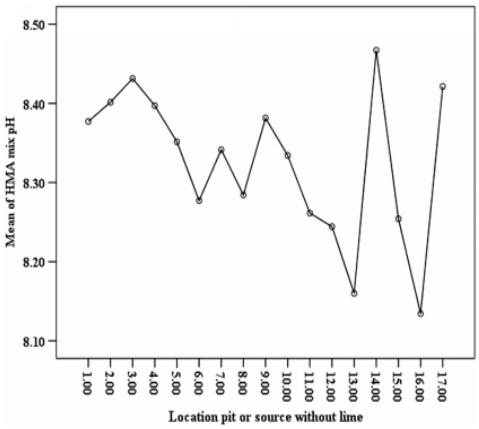

Fig. 6. Mean plot of HMA mix without lime versus location pit or source

lime added. It should be noted the aggregate chemistry at these locations, coupled with lime, seem to be creating higher pH mean values.

Bivariate screening was completed to further investigate and look for any correlation between any other pairs of independent variables.

The independent variables found to be significantly correlated with HMA mix pH (at a 0.05 significance level) were as follows:

1. SiO_2, $r = -0.203$, $p = 0.002$;
2. $CaCO_3$, $r = 0.182$, $p = 0.005$; and
3. CaO, $r = -0.175$, $p = 0.007$.

According to the strength guidelines with Pearson correlations coefficient at 0.20 or less, the relationship is a very weak one and is even negligible. All these had p-values of less than 0.20 in the bivariate screening. The strongest relationship among the independent variables was between SiO_2 and $CaCO_3$. With a Pearson correlation coefficient of −0.854, this indicates that as SiO_2 increases, $CaCO_3$ decreases. They are too highly correlated for both to be present in a regression analysis, so a variance inflation factor (VIF) will be computed to determine whether collinearity is a problem. CaO is strongly correlated with SiO_2: $r = -0.514$, $p = 0.000$.

As an important part of this analysis, one-way ANOVA tests were conducted on all variables to determine whether or not there were significant relationships between continuous and categorical variables. This made it possible to screen independent variables for possible inclusion in the multivariate model. The screening resulted in the following p-values, which were used in selecting the independent variable to include in the final multivariate regression model. The continuous and categorical variables found to have a significant p-value with lime were pit, binder, lime, region, pHagg_boiled, and formula, and without lime they were pit, oil, binder, region, pHagg_boiled and formula (Table 6).

Bivariate comparisons were made between all pairs of categorical variables in order to check for independence.

Pearson's chi-squared tests of independence were used to investigate whether distributions of categorical variables differed from one another. The eight categorical variables were pit, oil, binder, lime, PPA, time, region, and formula. None of the variables with p-values of 0 were independent of each other. Those variable pairs found not to be independent were, for example, pit/region, pit/formula, oil/time, and binder/PPA. These were identified so as to ensure that in multivariate regression work, no two highly dependent variables would be considered in a regression model simultaneously. These variables are bolded **0** in Table 7.

The mean pH levels were considered across all pits to see whether they were the same. This was done for pits with and without lime. Without lime the mean was 8.32, whereas with lime it was 8.98. Pits 13 and 16 (with lime) show mean pH values of 10.8 and 10.51. Levene's test showed the existence of unequal variances since Pit 3 had a standard deviation of 0.07, while Pit 16 had a standard deviation of 0.73, ten times greater. It is significant that the mean pH values from Pits 13 and 16 are so high.

A t-value of the paired pH samples for the 24 h soaking period versus the 48 h soaking period was computed (Table 8). The p-value of the correlations was 0.205. The t-value needed for rejection of the null hypothesis at DOF = 33, 0.05 two-tailed test is 2.03 (Salkind 2007). Therefore, the null hypothesis cannot be rejected, and the 24 h soaking period is adequate.

Table 6. Results of Bivariate Screening of Independent Variables against pH

Parameter	Variable	Type	*F*-statistic	*p*-value	Comments
With lime	Pit	Categorical	4.005	0	Include
	Oil	Categorical	0.215	0.643	Do not include
	Binder	Categorical	2.324	0.129	Include
	Lime	Categorical	90.294	0	Include
	PPA	Categorical	0.039	0.843	Do not include
	Time	Categorical	1.31	0.253	Do not include
	Region	Categorical	11.415	0.001	Include
	SiO_2	Continuous	6.996	0	Include
	$CaCO_3$	Continuous	3.68	0	Include
	CaO	Continuous	5.74	0	Include
	Al_2O_3	Continuous	5.74	0	Include
	MgO	Continuous	5.74	0	Include
Without lime	Pit	Categorical	3.644	0	Include
	Oil	Categorical	6.255	0.014	Include
	Binder	Categorical	6.078	0.015	Include
	PPA	Categorical	0.556	0.458	Do not include
	Time	Categorical	22	0	Include
	Region	Categorical	8.51	0.004	Include
	SiO_2	Continuous	6.996	0	Include
	$CaCO_3$	Continuous	3.68	0	Include
	CaO	Continuous	5.74	0	Include
	Al_2O_3	Continuous	5.74	0	Include
	MgO	Continuous	5.74	0	Include

Table 7. Chi-Square Tests of Independence

Parameters	Chi-square	DOF	*p*-value
Pit, oil	0	16	1
Pit, binder	0	16	1
Pit, lime	0	16	1
Pit, PPA	0	16	1
Pit, time	0	16	1
Pit, region	238	16	**0**
Pit, formula	2,618	176	**0**
Oil, binder	1.983	1	0.159
Oil, lime	0	1	1
Oil, PPA	1.983	1	0.159
Oil, time	29.75	1	**0**
Oil, region	0	1	1
Oil, formula	0	11	1
Binder, lime	0	1	1
Binder, PPA	38.08	1	**0**
Binder, Time	15.867	1	**0**
Binder, region	0.000	1	1
Binder, formula	0.000	11	1
Lime, PPA	0.000	1	1
Lime, time	0.000	1	1
Lime, region	0.000	1	1
Lime, formula	0.000	11	1
PPA, time	15.867	1	**0**
PPA, region	0.000	1	1
PPA, formula	0.000	11	1
Time, region	0.000	1	1
Time, formula	0.000	11	1
Region, formula	209.100	11	**0**

Note: DOF = degrees of freedom. Bold values indicate that never use both variables in a model simultaneously.

Because the research question contains more than one variable, multivariate analysis of variance, which looks at group differences but controls the relationship between the independent variables, will be used to evaluate the objectives of this study.

Table 8. Paired Sample Test Results

Parameter	Value
Pair	pH-pH
Mean	−0.04735
SD	0.21343
t	−1.294
DOF	33
Significance or *p*-value (two-tailed)	0.205

Note: DOF = degrees of freedom.

The final multivariate linear regression model was developed by first including all variables found to be significantly related to pH at an alpha of 0.15 in the bivariate screenings and then reducing the model to one in which only variables significant at an alpha of 0.05 remained. This was done for the models with and without lime. With all other variables held constant, the level of SiO_2 was found to be significantly correlated to the pH of the HMA mix, $F \times (9,218) = 41.176$, $p = 0.000$. The size of the effect was such that, on an average, every one-unit increase in SiO_2 was associated with an increase of pH of 0.916 units, with hydrated lime being the primary contributor at 8.892 units. Since pH is a logarithmic scale, more research needs to be done on the extent and significance of the numbers obtained since going from an 8.5 pH to an 11 pH is a 2.5×10-fold or 25-fold increase in the concentration of hydrogen ($H+$) ions. A literature review revealed that as $H+$ ions increase, the pH tends to vary toward an acidic concentration of ions, and calcium dissolution can take place in a pH range of 1–6. It is deduced that this pH change may be localized and site specific with the reactive aggregate. The silicate lattice reaction with water imports excess hydroxyl ions, which is a typical hydrolytic reaction of the salt of a weak acid (Little 2003). This would explain that from the chemical formulas, silica dioxide at 20–48% with various percentages of calcium carbonate, calcium oxide, magnesium oxide, and aluminum trioxide, at 42–80%, may be producing acidic reactions and changing the pH levels.

Both residual plots and fit statistics indicate that the final models were poorly fit but have approximately 47–50% explanation value (with lime) or no value (without lime), because the algorithm broke down, in accounting for the chemical reaction at the asphalt binder/aggregate interface.

Using the general linear model, analyses were run with lime, with the following results:

From the main effect's model it was determined that CaO (with a *p*-value of 0.64) could be dropped, leaving hydrated lime and SiO_2 as variables to be used in the model because all others were statistically eliminated. (Hydrated lime: $F = 123.93$, $p = 0.000$; and SiO_2: $F = 10.77$, $p = 0.000$).

From this analysis, as was noted earlier, the addition of lime accounted for ALL of the samples in which the pH exceeded 9. This appears to be a primary factor affecting the pH of the final mix.

Note that all variables that remain in the model are significant with all *p*-values reported as 0.000.

Using the general linear model, analyses were run on data without lime, with the following results:

From the main effect's model for data without lime it was determined that $CaCO_3$ was redundant and SiO_2 was significant, so SiO_2 was used in the model because all others were statistically eliminated; $SiO_2 - F = 4.454$, $p = 0.000$.

Assessing the strength of the model with lime:

The Shapiro–Wilk test, used to assess whether or not residuals are normally distributed, will be used to check the residuals. This test detects departures from normality due to skewness, kurtosis, or both.

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The plot of predicted versus observed values was scattered and did not line up in a straight line and do not look good for fit. The model is not good for making predictions or inferences: $F \times (9,218) = 41.176,\ p = 0.000$.

Assessing the strength of the model without hydrated lime:

The plot of predicted versus observed values was also scattered and did not line up in a straight line and does not look good for fit. The dots present in the output table mean that the test was unable to run because the algorithm broke down. Nothing can be taken from this model.

Tests of between-subject effects and parameters are shown in Tables 9–12, leading to mathematical models.

The tests of between-subject effects resulted in a value of 0.493 (adjusted R-squared value of 0.471). This R value indicates that this model explains 47–49% of the observed variation in the final pH levels.

From parameter estimates, when SiO_2 is held constant, at a 20% level of SiO_2, on average there is a decrease in pH of 0.652 units.

The 95% confidence interval for this decrease is (0.537, 0.768). When controlling for the addition of lime, at $SiO_2 = 0.20$ or 20%, there is an increase in pH of 0.916 units. The 95% confidence interval for this increase is (1.191, 0.642) and at $SiO_2 = 0.48$ or 48% is associated with a 0.761 increase in pH. The 95% confidence interval for this increase is (1.035, 0.486).

The tests of between-subject effects without lime resulted in a value of 0.269 (adjusted R-squared = 0.209).

This R value indicates that this model explains 20–27% of the observed variation in pH levels.

Through a manual optimization procedure a statistically significant model was developed for relating pH to two and one independent variables. Mathematically the models take the form

$$\text{pH} = 8.892 - 0.652(\text{lime}) + 0.916(\text{SiO}_2) \quad (1)$$

$$\text{pH} = 8.369 + 0.099(\text{SiO}_2) \text{ at } 0.59 \quad \text{or} \quad 59\%(\text{without lime}) \quad (2)$$

SiO_2 is a continuous variable whose value ranged between (0.2 or 20%, 0.82 or 82%) as used in this research study. No attempt should be made to extrapolate outside of these ranges. Lime assumes a value of 1 when it has been added to the mix and 0 otherwise. The model is assessed as being poorly fitting but, from R-squared = 0.493 (adjusted R-squared = 0.471), explains approximately 47–49% of the pH variation, and caution should be used for prediction purposes.

The biggest determinant of whether or not pH will exceed a value of 9.0 appears to be whether or not hydrated lime is added. Among the 238 samples examined in this analysis, there were no

Table 9. Tests of Between-Subject Effects with Lime

Dependent variable: pH of HMA mix with lime								
Source	Type III sum of squares	DOF	Mean square	F	Significance	Partial eta squared	Noncentrality parameter	Observed power[a]
Corrected model	45.091[b]	10	4.509	22.084	0.000	0.493	220.841	1.000
Intercept	14,024.770	1	14,024.70	68,689.061	0.000	0.997	68,689.061	1.000
Lime	25.303	1	25.303	123.929	0.000	0.353	123.929	1.000
SiO_2	19.787	9	2.199	10.768	0.000	0.299	96.912	1.000
Error	46.348	227	0.204	—	—	—	—	—
Total	17,902.360	238	—	—	—	—	—	—
Corrected total	91.439	237	—	—	—	—	—	—

Note: DOF = degrees of freedom.
[a]Computed using alpha = 0.05.
[b]R-squared = 0.493 (adjusted R-squared = 0.471).

Table 10. Parameter Estimates with Lime

Dependent variable: pH of HMA mix with lime									
					95% confidence interval				
Parameter	B	Standard error	t	Significance	Lower bound	Upper bound	Partial eta squared	Noncentration parameter	Observed power[b]
Intercept	8.892	0.076	117.576	0.000	8.743	9.041	0.984	117.576	1.000
[Lime = 0.00]	−0.652	0.059	−11.132	0.000	−0.768	−0.537	0.353	11.132	1.000
[Lime = 1.00]	0[a]	—	—	—	—	—	—	—	—
[$SiO_2 = 0.20$]	0.916	0.139	6.572	0.000	0.642	1.191	0.160	6.572	1.000
[$SiO_2 = 0.31$]	−0.093	0.110	−0.842	0.401	−0.310	0.124	0.003	0.842	0.134
[$SiO_2 = 0.40$]	−0.071	0.139	−0.507	0.613	−0.345	0.204	0.001	0.507	0.080
[$SiO_2 = 0.48$]	0.761	0.139	5.455	0.000	0.486	1.035	0.116	5.455	1.000
[$SiO_2 = 0.49$]	−0.010	0.139	−0.072	0.943	−0.285	0.265	0.000	0.072	0.051
[$SiO_2 = 0.59$]	0.059	0.139	0.425	0.671	−0.215	0.334	0.001	0.425	0.071
[$SiO_2 = 0.68$]	0.162	0.110	1.468	0.144	−0.055	0.379	0.009	1.468	0.309
[$SiO_2 = 0.72$]	−0.042	0.092	−0.452	0.651	−0.223	0.140	0.001	0.452	0.074
[$SiO_2 = 0.75$]	−0.181	0.139	−1.296	0.196	−0.455	0.094	0.007	1.296	0.252
[$SiO_2 = 0.82$]	0[a]	—	—	—	—	—	—	—	—

[a]This parameter is set to zero because it is redundant.
[b]Computed using alpha = 0.05.

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Table 11. Tests of Between-Subject Effects without Lime

Dependent variable: HMA mix without lime					
Source	Type III sum of squares	DOF	Mean square	F	Significance[a]
Corrected model	0.735b[a]	9	0.082	4.454	0.000
Intercept	6,377.533	1	6,377.533	348,055.974	0.000
SiO_2	0.735	9	0.082	4.454	0.000
Error	1.997	109	0.018	—	—
Total	8,249.518	119	—	—	—
Corrected total	2.732	118	—	—	—

Note: DOF = degrees of freedom.
[a]Computed using alpha = 0.05.
[b]R-squared = 0.269 (adjusted R-squared = 0.209).

Table 12. Parameter Estimates without Lime-Dependent Variable: HMA Mix without Lime

					95% confidence interval	
Parameter	B	Standard error	t	Significance	Lower bound	Upper bound
Intercept	8.369	0.030	283.308	0.000	8.310	8.427
[$SiO_2 = 0.20$]	−0.209	0.059	−3.530	0.001	−0.326	−0.091
[$SiO_2 = 0.31$]	−0.053	0.047	−1.132	0.260	−0.145	0.040
[$SiO_2 = 0.40$]	−0.034	0.059	−0.580	0.563	−0.151	0.083
[$SiO_2 = 0.48$]	−0.234	0.059	−3.966	0.000	−0.351	−0.117
[$SiO_2 = 0.49$]	0.053	0.059	0.895	0.373	−0.064	0.170
[$SiO_2 = 0.59$]	0.099	0.059	1.669	0.098	−0.019	0.216
[$SiO_2 = 0.68$]	−0.056	0.047	−1.193	0.235	−0.148	0.037
[$SiO_2 = 0.72$]	−0.024	0.039	−0.612	0.542	−0.101	0.054
[$SiO_2 = 0.75$]	−0.107	0.059	−1.814	0.072	−0.224	0.010
[$SiO_2 = 0.82$]	0[a]	—	—	—	—	—

[a]This parameter is set to zero because it is redundant.
[b]Computed using alpha = 0.05.

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instances where lime was not added and the mix exhibited high pH values.

The results point to aggregate chemistry as explaining pH values between 8.495 pH, the median of this study with lime, and 9.0 pH, the value at which every pH above it had lime added. This is significant in some locations or sources when adding lime because as together they may increase the chance of chemical reaction affecting adhesion. Aggregate properties have a greater impact on pH values than do various asphalt binder formulations. An analysis of oil type showed that 70-28 was not significant, but 64-34 was close to having 95% confidence.

The first objective was to investigate the relationships between the components used in the HMA mixes in order to determine their individual contribution to the final pH within the HMA mixes. The chemistry of the aggregate can, when combined with lime and moisture, create a pH environment at the asphalt binder/aggregate interface conducive to chemical reaction, leading to the bond's being compromised. The overall biggest factor affecting final pH is the addition of hydrated lime to the HMA mix, which is to be expected. In this study, those mixes to which hydrated lime had been added exhibited a higher mean pH value but also tested with a much greater variability. Aggregate components, such as SiO_2, $CaCO_3$, and CaO, had an effect on the final pH and added or subtracted from the final analysis. Knowledge of the aggregate chemistry and its potential to react with lime would improve the overall success of bonds and a longer-lasting pavement. ASR/ACR should be investigated in suspect pits.

The second objective was to determine whether the final pH of a HMA mix was a significant predictor of chemical reaction, which may lead to stripping damage in the asphalt binder/aggregate mix. The issue of stripping damage has not been evaluated in this work.

Hydrated lime has a direct effect on the final pH of a HMA mixture of materials and, when combined with certain percentages and types of silica and carbonates, can increase or decrease the pH level. The use of hydrated lime in most mixes (85–90%) helps bonding and improves adhesion. In 10–15% of mixes, the chemistry of the aggregate factors into the equation and, combined with the lime, creates chemical reactions in the mix, as indicated by exchanges of $H+$ ions and $OH-$, causing an unstable interface between the asphalt binder and the aggregate. Higher pH values are predictive of detrimental chemical reactivity in the asphalt binder/aggregate mix.

The first research question was whether the pH of individual components of aggregates, asphalt binder, and additives point to and isolate suspect materials that chemically react and affect the final pH value.

Components such as hydrated lime, which is an additive, moisture, and the chemistry of the aggregate (SiO_2, $CaCO_3$, and CaO) had the most significant effect on the final pH value. The chemical composition of the aggregate in the source pit will have a positive or negative effect on the pH value depending on the percentages of each mineral.

The second research question was whether the final pH levels of mixed HMA materials (asphalt binders, additives, and aggregates) are significant in predicting chemical reaction, which is suspected to affect the durability of asphalt binder/aggregate mixes.

Higher final pH values are predictors of chemical reaction, and those that seemed to be outliers are the significant pH values that indicate that other components are contributing to the chemical reaction, resulting in varied (lower or higher) final pH values.

Conclusions

The research scale in this study was large, with many categorical and continuous variables. Successful analysis of the data with any degree of accuracy, required assessing the output of the statistical data to eliminate collinearity and redundancy of the variables. Many of the categorical variables were, at inception, set up to be independent. The categorical and continuous variables were dependent, independent, or confounded by the analysis and resulted in statistical elimination of most of them.

The chemical analysis of the aggregate varied over 17 sources and was not consistent in any of those sources. But through the statistical analysis, several chemical formulas stood out as potentially reactive aggregate sources. The mean pH was significant in pits with and without lime, and lime was present in every reading above 9 pH. The aggregate chemistry in each pit may account for the variation in pH of the HMA mix above 9 pH. A good amount of disparity was found between the mixes with lime and those without lime. Numerous outliers were observed when lime was added and created a right-tailed histogram and bell curve. These outliers were almost exclusively associated with Pits 13 and 16. Pit 15 had these same characteristics, but to a lesser degree.

The conclusion arrived at in connection with the first research question is as follows. The null hypothesis would be rejected because the final pH is dependent on the chemical reactions that take place at the asphalt binder/aggregate interface. The percentages of, for example, silica, carbonate, magnesium, and aluminum in the aggregate, along with the hydrated lime, affect the final pH value of the HMA mix.

The conclusion arrived at in connection with the second research question is as follows: the null hypothesis would be rejected because, through a manual optimization procedure, a statistically significant mathematical equation has been developed that relates pH to two independent variables and one independent variable. The final pH value depends on the chemistry of the aggregate, with the addition of lime appearing to have the largest effect.

Various authors have concluded that a thin molecular layer of water remains on the aggregate (Atkins 2003). It would take temperatures higher than 500°C to burn off the last molecular layer of moisture (Little 2005). Since the highest temperature used in a hot mix plant producing asphalt is 135–145°C, it is evident that moisture remains on the aggregate. Additional research needs to be done on the effect of temperature on the components of a mix. Since reactions can take place when moisture is present, research is needed to assess the temperature range needed to eliminate the last molecular layer of moisture to allow asphalt to bond more firmly with the rock surface without water present.

This would eliminate one simply neglected or ignored source of moisture that may cause pH instability to precipitate at the interface.

More research is needed on the interface of the asphalt binder and the aggregate with lime and without lime, considering the chemistry of the aggregate and varying it with more silica and less calcium to more calcium and less silica on a reactive level to determine whether pH changes from alkaline to acidic.

Further investigation using one or two control pits that produce stable HMA mixes should be carried out to compare suspect pits, such as Pits 13, 15, and 16 from this study, with high pH values and known HMA mix failures. The reasons for the high pH values found in the mixes in which lime had been added to HMA mixes from Source Pits 13, 15, and 16 should also be investigated. The chemistry of the rock found in those sources and their effects when combined with hydrated lime in different percentages could help to determine and isolate the underlying reasons for the anomalies found in the statistical analysis and stated in the conclusions presented in this paper.

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